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GREETINGS TO COMRADE J. V. STALIN

FROM THE ACADEMY OF SCIENCES OF THE USSR

Dear and Warmly Beloved Joseph Vissarionovich!

On the day of your seventieth birthday the Academy of Sciences of the Union of Soviet Socialist Republics sends you, the great helmsman of the country of socialism, its ardent and heartfelt greetings.

In you, the Academy of Sciences greets the fighter, the thinker, the scholar, whose entire life has been devoted to the revolutionary struggle for the liberation of the working class and all the toiling masses, the sage teacher and leader of the heroic party of the Bolsheviks, of the Soviet people, and of all progressive humanity.

With each new day there stand more clearly evident to the laboring masses of the entire world the great historic feats which you have achieved and are achieving in the struggle for the triumph of the cause of socialism, peace, and democracy, for the building of a happy and joyful life on earth.

The Great October Socialist Revolution, which became a reality to the peoples of Russia under the inspired leadership of Lenin and Stalin, has opened a new era in the development of human society, an era of the downfall of capitalism and the triumph of socialism, an era which denotes the beginning of the true history of humanity.

Under your wise guidance socialism has been built in our country and a decisive victory has been won over fascism in the Great Patriotic War; this victory has opened the path to the triumph of the peoples' democracies in a number of countries of Europe and Asia, a path to the construction of a powerful camp of peace, socialism and democracy, now uniting more than 800 million human beings.

The world-historic victory of socialism, and the successful advance of our people along the path to communism are the greatest triumph of the Marxist-Leninist science which teaches of society, of the laws of proletarian revolution, of the construction of socialism and communism. You are creatively developing Marxism-Leninism and are arming our cadres with this all-conquering doctrine, you are guiding us by the transforming power of Marxism in life.

On the foundation of the great Leninist-Stalinist theory of the possibility of the triumph of socialism in our country, the Soviet people have built the first powerful socialist state in the world. The great Leninist-Stalinist ideology of equal rights and friendship between peoples has found its incarnation in the building of the powerful multinational Union of Soviet Socialist Republics.

You, dear Comrade Stalin, like the deathless Lenin, are the light and hope of all progressive humanity. We are proud of the fact that we live in the Stalinist epoch — an epoch of the building of communism.

For Soviet scholars, your labors of genius and all your activity,

Joseph Vissarionovich, are the inexhaustible source of creative inspiration.

You are teaching the men and women of Soviet science the profound principles of creative boldness, of merciless struggle against routine and stagnation. You are educating our scholars in a feeling of lofty responsibility to our country, and to our people for the development of Soviet science. Your historic direction to the scholars of our country – not only to reach, but to surpass in the shortest possible period the attainments of science abroad – has inspired all the workers in science with new energy, with the striving to press indefatigably forward to new successes.

Soviet science truly serves to strengthen the power of our Fatherland, revealing and utilizing the countless natural treasures of our country. Soviet science serves the cause of peace and the prosperity of our Fatherland, it develops on the firm foundation of the great doctrine of Lenin and Stalin, it is doing and will continue to do its share in the historic cause of building communism. Thanks to your unvarying attention and care, extremely favorable conditions have been created for the flourishing of every variety of progressive science in the Soviet Union, for the creative friendship of science and practice, for the most rapid scientific generalization of the experience of progressive practice and the installation in industry of the achievements of science.

The Academy of Sciences of the Union of Soviet Socialist Republics is proud, dear Joseph Vissarionovich, that you are an honorary member of our Academy.

The Academy of Sciences of the USSR and the entire army of Soviet scholars are happy that in our country of victorious socialism, science, in accordance with your directive, is actually serving the people, basing itself on the tasks of elevating the well-being of the toiling masses, on the interests of protecting peace. And with a feeling of great admiration, we, the scholars, are continually convinced of the fact that there is not a single branch of science and culture where your guiding thought is not expressed, where your creative genius is not reflected.

We send you our heartfelt greetings, dear Joseph Vissarionovich, on the day of your seventieth birthday; we express our feeling of gratitude; we extend to you our warm wishes for many, many years of life and health for the welfare and the glory of our great Fatherland, for the happiness of the laboring masses of the entire world.

Long live our beloved teacher and leader, the glory of the Soviet people, the pride of Soviet science – the great Stalin.

Discussed and accepted by the participants at a general meeting of the Academy of Sciences of the USSR

CHARACTERISTIC FEATURES OF THE DEVELOPMENT OF CHEMISTRY IN THE USSR IN THE YEARS OF THE STALIN FIVE-YEAR PLANS

S. N. Danilov

The Great October Socialist Revolution made a basic change in every aspect of our country's life, revealing broad possibilities for its economic and cultural growth. In the very first years of Soviet power, on the initiative of the organizer of the Soviet state, V. I. Lenin – the genius of the revolution, the coryphaeus of science, the greatest human being of modern times – powerful measures were adopted for the development of education and general culture, and for the raising of the level of the people's economy of our Fatherland to a height unequalled in the past. And this was despite the difficult conditions in which the Republic of Soviets then found itself as a result of the fierce struggle with the white-guardists and the interventionists.

But the extremely rapid development of industry and agriculture was accompanied by the widespread establishment of a network of schools, institutions, of higher learning, and scientific establishments, which was begun in particular after the time when Joseph Vissarionovich Stalin, the great continuator of Lenin's cause, set before the XIVth session of the Communist Party in December, 1925, the task of converting the Soviet Union from an agrarian country, with a backward technique, into an industrial country, with a powerful industry and large-scale agriculture.

The rise and development of industries, among them the chemical industry, which was begun in 1922, when the young Soviet Republic was devastated by enemies who had set upon it from all sides, attained very great momentum from the time of the historic speech of Comrade Stalin at the XIVth session of the party. In the following years (1925-1929) which were a sort of preparatory period for the remarkable Stalin Five-Year Plans for the development of the people's economy, much was already achieved, both in raising our industry and agriculture to a higher level, and in the preparation of personnel as specialists of different kinds.

At the XVth session of the Party in 1927, J.V.Stalin designated as our main task the collectivization of agriculture. The most important condition of this noteworthy plan for the transformation and development of agriculture was the widespread introduction of agricultural machines, on the basis of a broad development of metallurgy and machine construction, and of artificial chemical fertilizers.

In the development of chemical science and chemical industry, a great role was played by the decree of the Council of Peoples Commissars of April 28, 1928 on the formation of a Committee to introduce chemistry into the peoples' economy, in particular on the wider dissemination of scientific-research work in the field of chemistry, leaving large-scale methods aside.

From 1929 on our country entered, as Comrade Stalin had directed, on the path of fulfillment of the great Five-Year Plans for development of the peoples' economy.

The greatest of scholars, J.V.Stalin, developed the path and the most important conditions for the socialist industrialization of our country and for the collectivization of agriculture; he was the initiator, the inspirer, and the guide in the construction of new branches of industry, of a great number of new factories and mills, of new industrial towns and regions.

In April, 1929, the XVIth party conference adopted the first Five-Year-Plan for the development of industry and agriculture.

After the first Five-Year Plan (1929-1933), actually before the period was completed, there followed a second extraordinarily fruitful Five-Year Plan for the peoples' economy; this was completed in April, 1937, after 4 years and 3 months.

In accordance with the resolution of the XVIIth session of the CPSU (Bolsheviks), which was, "To produce decisive shifts in the development of chemical industry, to secure the widespread introduction of chemical methods into all branches of the peoples' economy, and to strengthen the defensive capacity of the country", by the end of the second Five-Year-Plan great progress had been made in the hard coal, slate, and petroleum industries, in ferrous metallurgy (smelting of cast iron and steel, high quality rolled iron), in non-ferrous metallurgy (copper, aluminum, nickel, tin), in fertilizers, in the nitrate industry, in synthetic rubber, artificial fibers, plastics, and in many other branches of production.

The end of the second Five-Year Plan was made noteworthy by the declaration on December 5, 1936 at the XVIIth session of the Soviets of the Stalin Constitution, which noted the honorable rights and obligations of a Soviet citizen, summed up the progress made in socialist construction, ans set up stable foundations for the building of a communist society. As a result of the successful completion of the first and second Five-Year Plans, our Fatherland was converted into a country which had by its own means supplied its economy and defense with all necessary technical equipment. In 1933, Comrade Stalin could already say: "Nor did we have a major chemical industry. Now we have one".

In 1938, at the XVIIIth session of the CPSU(B), a proposal was developed with regard to the third Five-Year Stalin Plan for the development of industry and agriculture. The third Five-Year Plan was carried out under the slogan of paying especially great attention to the needs of extending chemistry through the country: "The third Five-Year Plan is a chemical Five-Year Plan." The progress of chemical methods as a result of the first and second Plans was to be greatly multiplied as a result of the third Plan for the economy. Its successful completion was prevented by the bandit onslaught of the fascist hordes upon the Land of the Soviets.

After the victorious conclusion of the four-year Patriotic War, our Fatherland, under the wise guidance of Comrade Stalin, advanced toward the fulfillment of the postwar Five-Year Plan for the reconstruction and development of the national economy. In the years of this Plan, great and complicated tasks were set before chemical industry with regard to its further large-scale growth. At the same time, honorable tasks were set before those active in science and technology. In Point 3 of the Decree on the postwar Five-Year Plan, adopted by the Supreme Soviet of the USSR on March 18, 1946, it was noted: "In order to provide the utmost in technical progress for all branches of the peoples' economy of the USSR, as a condition for the mighty upsurge of production and the increased productivity of labor, it is necessary not only to reach, but to surpass in the shortest possible time the attainments of science beyond the borders of the USSR."

The postwar Five-Year Plan for the reconstruction and development of the peoples' economy has already been completed with regard to many important tasks. The last year of this plan – 1950 – offers a clear index of the powerful development of all branches of life in our Soviet fatherland. Soviet chemistry is laboring with honor for the completion of the Five-Year Plan for the chemical industry.

During the time of the Stalin Five-Year Plans for the peoples' economy, under the guidance of the great Stalin, the greatest successes have been attained in chemical industry and in chemical science, inseparably bound to each other.

Chemistry, like all other sciences in the USSR, is being developed on the basis of dialectical materialism, so remarkably enriched and applied with such genius by V.I.Lenin and J.V.Stalin.

It is easy to observe a series of characteristics in the development of chemical science in the USSR in the Leninist-Stalinist epoch, and especially in the years of the great Stalinist Plans.

Let us enumerate several general characteristic features in the development of Soviet chemistry:

1. The characteristics of Soviet science are determined by the structure of our state, by the laws inscribed in the Stalin Constitution, by the tasks of socialist construction; it is a fundamental section of the state. Science in the Soviet state knows no rivalry and no planlessness, it belongs to the entire people. All this is true in every respect of chemistry too.

2. The broad scope of scientific research in the various sections of chemistry is possible because of the rapidly growing personnel in chemical science, who are developing large-scale collective projects of scientific and technical knowledge; the different scientific disciplines are confronted with profound questions, of importance to the solution of definite practical problems. The planning of scientific research work according to five-year and one-year periods makes its accomplishment very successful.

3. A many-sided theoretical study of naturally and artificially obtained substances is founded on a wide range of raw materials, of value to the peoples' economy either at the very moment or in the future. During the time of the Stalin Plans a huge broadening of the raw material basis for chemical industry was accomplished.

4. The high theoretical level of scientific research, with a broad examination of the problems raised, profound theoretical acuteness on the one hand, and on the other, the detailed treatment of technical problems on the basis of theoretical data.

5. The close ties between scientific investigations, with their high theoretical level, and daily practical problems, the demands of industry, agriculture, medicine, etc.

6. The characteristic that practice and theory, as they should be, are mutually related: scientific achievements receive practical application, and the needs of practice evoke theoretical problems.

7. The direct ties between the widely developed chemical research and the increasing number of scientific chemical establishments and chemical personnel with the tasks of completing the Stalin Five-Year Plans become all the more numerous as the Five-Year Plans for the peoples' economy set clearly outlined problems to scientific-technical thought.

8. The much-broadened flow of scientific chemical investigation, expressed, among other ways, by the enormous growth in the number of scientific conferences, chemical journals, articles, books on specific problems, etc., compared to the situation before the Stalin Plans.

9. The rapid application of scientific achievements in practice this was impossible in pre-Revolutionary Russia. As an indication of this, it is sufficient to recall that as a result of the tireless zeal of Comrades S.M. Kirov, G.K.Ordzhonokidze, and in particular of Comrade Stalin, the synthetic divinyl-rubber of S.V.Lebedev traveled the road from laboratory specimens to large-scale factory production in a period of about three years in all.

10. Soviet chemistry travels its own paths, and taking part in the general development of world science, adds to the latter the very great acquisitions made during its development; in a number of instances it has made discoveries and achieved results which have pointed out new paths for chemical science.

11. New Soviet schools have been founded in the most important branches of chemistry. There is a clear organic connection between the work of the Soviet chemical schools and the work of the Russian chemical schools of the pre-Revolutionary period, but of course with those changes in the direction of investigation which have been evoked by the characteristics of the Stalinist epoch; there is no cause for wonder in this, as chemistry is an experimental science, and new schools and directions follow from earlier existing schools.

Russian chemistry, beginning with M.V.Lomonosov, has added valuable treasures to world science, in particular in the second half of the XIX century and in the XXth century (N.N.Zinin, A.M.Butlerov, D.I.Mendelyeev, and others).

Towards the time of the Great October Socialist Revolution, many famous schools of chemical science acquired great renown; their leaders, with great persistence and inspiration, have continued, and continue to work during the Soviet period of our science as well, their pre-Revolutionary activity being succeeded by work in Soviet chemistry (N.S.Kurnakov, A.E.Favorsky, N.Ya. Demyanov, N.D.Zelinsky, and many others).

From these schools have sprung young Soviet schools of chemical science, successfully aiding in the completion of the Stalin Five-Year Plan.

It is impossible, in a short article, to give much information about the scientific discoveries of Soviet chemists in even any single branch of chemistry during the extremely fruitful period of the Stalin Five-Year Plans.

The goal set for this article will have been attained if we succeed in showing, by means of several examples the great achievements made and the main features of Soviet chemistry in the Stalinist epoch. We shall take our examples from those groups of substances which have a very important raw material base, a base which has been greatly broadened during the past 25 years and plays an extremely important role in the glorious industry of our Fatherland.

Naturally, the things that are of chief importance with regard to resources and means of production are mineral substances, particularly the metals, ferrous and non-ferrous, and inorganic salts and acids, which find application in industry in huge quantities and as chemical fertilizers for collective farms.

We shall draw our examples from the chemistry of carbon, and in particular we shall review briefly, in the first place, the successes in the field of hydrocarbons, with special emphasis on the chemistry of petroleum and chemical rubber, and in the second place the chemistry of oxygen and nitrogen compounds, such as: sugars and polysaccharides (cellulose), and protein. Despite essential differences

in composition and properties, all these groups of compounds are characterized by certain bonds of relationship. These carbon compounds are of fundamental importance in broad branches of chemical industry, especially those developed during the years of the Stalin Five-Year Plans. Because of the diversity of their forms and properties, these compounds are also of much interest, and contribute a great deal to the development of our views in the field of organic chemistry.

I. The Chemistry of Hydrocarbons in Relation to the Chemistry of Petroleum and of Synthetic Rubber

The widespread distribution and availability of hydrocarbons, their great practical value, the simplicity of their composition, and consequently the great possibilities of explaining the characters of hydrocarbon chains (straight, branching) or hydrocarbon rings, with simple and multiple bonds, and in addition the properties of the hydrogen atoms attached to a chain or ring – all these factors make this group of organic compounds extremely interesting. The chemistry of hydrocarbons has now become a very broad field. The richest source of hydrocarbons is in crude oils.

We are especially interested in those reactions of petroleum hydrocarbons which offer the possibility of altering the nature of the hydrocarbons; this is done because of its special value as a component of motor and other fuels, or as a means of its utilization for syntheses of great technical value.

The question of the composition of petroleum is of especially great interest; so is the question of changing its composition by means of chemical action, as for example, in order to increase the anti-detonation properties and to increase the amount of aromatic hydrocarbons.

This refers primarily to the paraffin, naphthenic, and aromatic hydrocarbons of petroleum and in part to natural gases.

Hydrocarbons with one or two multiple bonds, especially those obtained by the decomposition (pyrolysis, cracking) of petroleum hydrocarbons, attract great interest as starting materials for the production of synthetic rubber and other high polymers.

We may recall here the ever growing value of polythene, polyisobutylene, butyl rubber, and the different synthetic copolymerized rubbers.

Among the hydrocarbons with triple bonds, acetylene has long had great technological value, but more recently the ethylene acetylenes have also become important, as a result of their utilization by way of their halogen derivatives in chlor rubbers. However, "wood acetylene", which is now so widely used, will be treated only partially in this article, in view of the fact that it is based on the use of calcium carbide, and is apart from the chemistry of petroleum and the rubbers (not counting chloroprene).

Of those purely biochemical and physiological substances which appear, according to our present state of knowledge, to be characteristic of the organism, none seem to be related to the hydrocarbons. However, hydrocarbons are produced in plant organisms; we may refer to the terpene hydrocarbons and to rubber, (which is based on isoprene), both of which play other, chiefly protective, roles in plants.

Petroleum is related to the substances of the animal and plant world in the sense that it was formed from them over extended geological periods. There is thus a relationship in origin, despite the profound difference in properties,

between the hydrocarbons of petroleum and the compounds of a carbohydrate and protein nature.

As the result of a combination of oxidation-reduction transformations, a great number of plant residues have been converted by oxygen, in the course of geological ages, along complicated paths, into numerous hydrocarbons of different molecular weights and different structure, [1].

Butlerov and his students did a tremendous amount to explain the structures and properties of hydrocarbons. Isomers of the saturated and ethylenic hydrocarbon series, predicted by Butlerov's structural theories, were synthesized and their structures clarified; these include, the structure of isobutane (by Butlerov), tetramethylmethane (M.D.Lvov), and isobutylene (Butlerov), etc.

The chemistry of acetylene and diene hydrocarbons has been developed by many of our chemists: A.P.Sabanyeev, A.P.Eltekov, M.G.Kucherov, and especially, A.E.Favorsky (from 1884), as well as S.V.Lebedev at a much later time.

Butlerov's students also tremendously enriched the chemistry of polymethylene hydrocarbons. The simplest rings and their transformations were successfully investigated by G.G.Gustavson, S.M.Tanatar, V.V.Markovnikov, M.I.Konovalov, N.Ya. Demyanov, N.M.Kizhner, A.E.Favorsky, and N.D.Zelinsky. Much of value in the chemistry of terpenes was accomplished by A.E.Vagner, F.M.Flavitsky, and in the last quarter of the century in particular, by S.S.Nametkin and others.

These famous pages in the history of Russian organic chemistry should not be forgotten. Many successes in these branches of chemical science in the Soviet period are connected with them.

In this article, with regard to the chemistry of the hydrocarbons, we shall first dwell on the most important reactions of petroleum hydrocarbons in relation to the problems of the enrichment of gasolines, and the methods of chemical rearrangement of the hydrocarbon raw material. We shall further consider progress in the chemistry of synthetic rubbers, which deserve great attention because of the fact that a synthetic rubber industry has quickly sprung up in the USSR on the basis of theoretical investigations in this field by our chemists, especially by S.V.Lebedev. This is a shining example of the fact that in our country, in the Stalinist epoch, very favorable conditions have been created for the development of our science and industry. The successes of the petroleum and synthetic rubber industries during the period of the Stalin Five-Year Plans have been astonishing. During these years, the combined forces of chemists and geologists have explored and brought into use many new petroleum deposits.

1. Investigation of Petroleum Hydrocarbons

In addition to the great wealth of petroleum which our Fatherland has possessed, many new petroleum regions were explored after the Great October Socialist Revolution. To the Caucasus and other petroleum-rich regions, there were added many others; for example, operations were begun in the Second Baku, and elsewhere.

In the past years, much work has been carried out in investigating the composition of petroleum in different regions, and in carefully extracting valuable fractions from the petroleum.

In the postwar Five-Year Plan (1946) on the reconstruction and development of the people's economy the broad task was set: "To develop the production of high octane aviation gasoline, to improve the quality of automobile gasolines, tractor kerosene, diesel fuel, and oils. To increase the yield of products from petroleum by means of cutting down on waste and widening the utilization of catalytic processes and other new methods of producing gasoline and technical oils."

During the Stalin Five-Year Plans, a great deal has been accomplished in the chemical re-formation of petroleum to give different chemical products. Even at the end of the last century, D.I.Mendelyeev urged the Tsar's ministers and industrialists that it was "time to remember that petroleum is not a fuel, but a valuable chemical raw material". In Soviet times, this thought of our great chemist has been realized in practice. As is known, petroleum contains hydrocarbons almost completely – paraffin, polymethylene (naphthene) and aromatic, with either paraffins or naphthenes predominating, and small admixtures of oxygen and sulfur-containing substances (the hydrocarbons constitute 99% of the petroleum).

Mixed naphthas (methanic-naphthenic-benzenic type) predominate; a small number of them are especially rich in paraffins, others in benzene hydrocarbons, all of them without fail contain naphthenes.

Natural gases (from gaseous and easily volatile paraffins) are beginning to have more and more value in our practice. The mineral resources of the USSR are rich in these.

The study of petroleum is closely related to the development of the chemistry of hydrocarbons.

Soviet chemistry can be proud of the fact that the earliest great successes in the investigation of petroleum, related in particular to the work of D.I. Mendelyeev, V.V.Markovnikov, M.I.Konovalov, N.D.Zelinsky, and others, have been multiplied to a tremendous extent in the Soviet period of our Fatherland.

Of no little significance are the methods of investigation of the chemical composition of petroleum and petroleum products.

Much had been done on this problem by V.V.Markovnikov [2] at the end of the past century, who had proposed methods for the investigation of petroleum products, and had applied direct distillation to the petroleums of the Caucasus. The method of M.I.Konovalov [3] was of great help in the investigation of petroleum; it involved the nitration of saturated and polymethylene hydrocarbons (naphthenes) with dilute nitric acid, followed by separation of the nitro compounds, which could be further converted into amines by the reaction of N.N.Zinin. Of the old methods proposed by Russian chemists, that of G.G.Gustavson deserves mention; it involved differentiation of the hexamethylenes by the action of bromine in the presence of aluminum bromide. This method was utilized by M.I.Konovalov [4] to characterize crude oils (for example, by this method methyl cyclohexane gives crystalline pentabromotoluene).

To distinguish the differences between the hexamethylenes and the pentamethylenes, there was a very valuable method by N.D.Zelinsky [5]; this depended on the absence of dehydrogenation in the pentamethylenes and paraffins and the taking place of dehydrogenation of the hexamethylenes to give aromatic hydrocarbons, which were further characterized by nitration, etc. (dehydrogenation catalysis of Zelinsky). To carry out the reaction, palladium black, heated to 300°, was convenient, as well as a nickel catalyst. By this method it was demonstrated that naphthenic acids did not usually contain the hexamethylene ring, probably as a result of the contraction of the original hexamethylene ring.

S.S.Nametkin and his coworkers [6] developed methods for determining unsaturated and aromatic hydrocarbons in cracked gasolines, the unsaturated being determined by treatment in the cold with sulfur monochloride, the aromatics in the usual way.

S.S.Nametkin's laboratory has developed group methods of analysis of crude oils, in particular a group analysis of the sulfur compounds in petroleum, and critically compared the different methods. Also very useful is the much earlier work of this author on the characteristics of petroleum products (1930).

As a supplement to distillation by means of improved columns, and methods of chemical analysis, such as nitration by Konovalov's method, dehydrogenation by Zelinsky's method, chlorination, sulfuration, action of sulfur at high temperature, etc., in the past years we have seen the widespread application of physical and physico-chemical methods of investigation, such as: the spectra of the combined scattering of light, a chromatographic method, etc. For example, in the laboratory of the Institute of Organic Chemistry of the Academy of Sciences, under the direction of B.A.Kazansky and G.S.Landsberg, there has been developed a complex method of detailed investigation of the individual constitutents of gasolines [7].

Much work has been done by Soviet chemists, as for example by S.S.Nametkin, one of the most important workers in the chemistry of terpenes and petroleum, on the investigation of different crude oils and natural gases.

The work on the composition of crude oils, carried out in the past century by such men as V.V.Markovnikov, N.D.Zelinsky, and others, is also being conducted at the present time, but to a much greater degree, with the synthesis of those components of the crude oil found or supposed to be present.

B.A.Kazansky [8] and his coworkers have synthesized the isomeric forms of hexane, pentane, and octane, in order that they might be studied in the laboratory of G.S.Landsberg by the spectra of combined scattering, in connection with the analysis of gasolines from crude oils of different origin. A.A.Petrov [9] has carried out a series of syntheses to obtain hydrocarbons of the composition C_{12} to C_{24} (about 50 syntheses), and has studied their properties, in particular the relation between anti-detonation properties and composition and structure.

Much more work has been done by our chemists on the chemical transformations of the hydrocarbons in petroleum, primarily on isomeric transformations.

The re-formation of the carbon skeleton of paraffins can be carried out with a variety of different conditions and catalysts. The transformation of a hydrocarbon skeleton into a more branched skeleton is of technical value, as this means an increase in the octane number of fuels. Our chemists have carried out a series of investigations on the isomerization of paraffins [9]. A.D.Petrov, I.Z.Ivanov, A.P.Meshcheryakov, and D.N.Andreyev have isomerized heptane and octane of normal structure in the presence of aluminum chloride, zinc chloride, and molybdenum sulfide. B.I.Moldavski and his coworkers have described the change of the hexane and octane skeletons in the presence of aluminum chloride, have studied the isomerization of butanes and pentanes in the liquid phase upon heating in the presence of aluminum chloride, and have examined the equilibrium relations of iso-hydrocarbons and the original butane and pentane. R.D.Obolentsev has studied the isomerization of liquid aliphatic hydrocarbons above fused aluminum chloride, and has carried out the transformation of hexane, heptane, and octane of normal structure into disubstituted hydrocarbons (dimethylbutane from hexane). According to the experiments of A.P.Sivertsev, the presence of aluminum chloride is favorable to the isomerization of n-heptane and n-octane.

These transformations of the carbon skeleton in n-octane are produced under conditions of dehydrogenation catalysis (platinum on activated carbon and nickel on aluminum oxide) in the experiments of Yu. K. Yuryev and P.Ya.Pavlov [10]. The thermodynamics of such transformations have been explained by A.V.Frost [11], in whose laboratory n-hexane has been isomerized over molybdenum disulfide into 2-methylpentane and 2,2-dimethylbutane.

In the group of oxidized organic compounds containing an open chain, the transformation into cyclic compounds of polymethylene, aromatic, and heterocyclic series has long been known. The formation of rings from acetylene and ethylene has also been known. But it has been discovered comparatively recently in the USSR

that saturated hydrocarbons are converted into aromatic hydrocarbons. This is of interest in relation to the problem of increasing the aromatic content of petroleum.

The reaction of dehydrogenating isomerization was discovered in 1930 simultaneously in several of our laboratories and can be of use in increasing the aromatic content of paraffin gasolines by catalytic methods.

B.L.Moldavsky, G.D.Kamusher, M.V.Kobilskaya, and F.Besprozvannaya produced ring formation from aliphatic hydrocarbons over amorphous chromium oxide at 460-470° [12].

B.A.Kazansky and A.F.Plate [13] have discovered that platinized carbon produces ring hydrocarbons from paraffins at 305 to 310°.

In the experiments of V.I.Karzheva, M.G.Severyanova, and A.N. Siova, paraffins were changed to aromatic hydrocarbons over a chrome-copper catalyst at 500 to 550° with some decomposition to lower products [14].

Earlier, in 1931, A.D.Petrov [15] obtained aromatic hydrocarbons in the form of mixtures by heating oleic acid at 380 to 400° under high pressure over aluminum oxide. A similar reaction for the formation of aromatic compounds from paraffins was investigated by B.A.Kazansky and A.F. Plate in a series of works [13].

The hydrocarbons of the ethylene series are easily isomerized, the double bond being shifted and the carbon skeleton altered. The double bond is displaced by the action of acid and alkaline agents, as was found long ago (A.P.Eltekov, F.M.Flavitsky, and A.E.Favorsky), and also under the conditions of heterogeneous catalysis, according to the experiments of our chemists in later years (N.D. Zelinsky, R.Ya. Levina, A.D.Petrov).

A.D.Petrov and V.I.Shchukin have found [16] that heptene-1 and octene-1 at high temperature and high pressure are converted into hydrocarbons with branched skeletons; the first into methyl diethyl ethylene, the second into dimethyl butyl ethylene. The isomerization [17] of butylene and isobutylene in the presence of clay and floridin has been described (A.V.Frost), as well as over aluminosilicate catalysts (G.I.Maslyansky, M.V.Veltistova). These reactions are of interest with regard to products of the cracking of petroleum.

It is well known that the saturated hydrocarbons can be dehydrogenated to give ethylene hydrocarbons, and the latter to give divinyls (according to the experiments of A.I.Yakubchik in the laboratory of S.V.Lebedev and in other laboratories).

The transformation of polymethylenes is of great interest for the chemistry of petroleum. They can be isomerized so as to narrow or widen the ring, changed to aromatic compounds, or split to give open chains.

The isomerization of polymethylene compounds with broadening or narrowing of the ring was first observed by Russian chemists (N.Ya. Demyanov, V.V.Markovnikov, N.M.Mizhner, and N.D.Zelinsky), who included in their observations the polymethylene hydrocarbons themselves.

Not long ago, M.B.Turova-Polyak [18] isomerized cycloheptane into methyl cyclohexane, and 1-methyl-2-ethyl pentane into 1,4- and 1,3-dimethyl cyclohexane over aluminum chloride.

Just as the action of hydrogen iodide on aromatic and polymethylene rings is accompanied by a change in the dimensions of the ring, aluminum chloride tends to transform polymethylene hydrocarbons by narrowing or broadening the rings, as has been found by numerous experiments of the school of N.D.Zelinsky. This is of interest in relation to the investigation of the transformation of ring groups.

Here, in passing, we must note that aluminum chloride, like sulfuric acid in the famous experiments of A.M.Butlerov on the polymerization of isobutylene, can be utilized to obtain synthetic gasolines, and synthetic lubricating oils or substances to be added to petroleum oils. S.S.Nametkin and his students have studied the chemical transformations produced by the action of these agents upon olefin hydrocarbons; polymerization was accompanied by hydrogenation-polymerization and dehydrogenation-polymerization. The polymerization of isobutylenes has been investigated similarly (S.S.Nametkin and M.G.Rudenko) [19].

A.D.Petrov and A.I Antsus and others have also studied the polymerization of ethylene, pseudobutylene, and the butylene fraction of pyrolysis gases under the action of aluminum chloride. From methane they were able to obtain acetylene, which, upon mixture with hydrogen, could be subjected to catalytic hydrogenation-polymerization to isobutylene in a kind of cross-polymerization, or to other ethylene hydrocarbon mixtures as a result of linear polymerization (Petrov, Antsus)[20].

It has long been observed that polymethylene hydrocarbons containing three-membered and four-membered rings undergo transformation into compounds of the ethylene series. The six-membered and five-membered rings are much more stable. However, it has been shown that the five-membered rings will undergo splitting under the conditions of catalytic hydrogenation, with formation of paraffin hydrocarbons (N.D.Zelinsky, B.A.Kazansky, A.F.Plate, S. Sergienko, Turova-Polyak, Denisenko, others.

Recently, the splitting reaction of cyclopentane hydrocarbons has been similarly studied by B.A.Kazansky and his coworkers [21].

The splitting of hydrocarbon bonds by means of hydrogen (hydrogenolysis) in the presence of hydrogenating catalysts depends upon temperature and the structure of the hydrocarbon.

The breaking of rings and paraffin chains was observed long ago in the presence of catalysts at high temperatures. For example, the destructive hydrogenation of petroleum is known from the work of various chemists (M.D.Tilicheyev, S.S.Nametkin, and others). Platinum catalyst does not usually split carbon bonds, especially paraffin bonds, even at 300°. Five-membered rings undergo hydrogenolysis in the presence of platinized carbon at 300 to 310°, with the formation of pentane of normal structure.

In the works of B.A.Kazansky on the cleavage of five-membered rings, a quantitative study has been made of all the products of reaction. In addition, the velocity of hydrogenation has been determined in the chief directions of reaction, and the role of the composition of substituents, of temperature, pressure, catalyst, etc. has been studied. Platinized carbon produces selective hydrogenation of the cyclopentane ring. A study has been made of the cleavage of ethyl cyclopentane, n-propyl cyclopentane, methyl cyclopentane, dimethyl cyclopentanes, and 1,2,3-trimethyl cyclopentane (the latter seemed more stable than the others). The easiest bond to break was the one situated across the carbon atom from those carbon atoms bound to substituents. Cyclopentane itself was the easiest of all to hydrogenate.

The catalytic dehydrogenation process of N.D.Zelinsky for transforming petroleum is of great interest. Although the reaction in which hydrogen is split off from cyclohexane and benzene is formed had been known at the beginning of this century, only in N.D.Zelinsky's investigations was it found to be of great value, both for organic synthesis, for distinguishing the size of rings in naphthenes and naphthenic acids, in particular, and also for the formation of aromatic hydrocarbons in petroleum. N.D.Zelinsky, Yu.K.Yuriev, and N.I.Shuykin showed (1934 and 1935) that by using catalytic dehydrogenation according to Zelinsky's method, it

was possible to increase the content of aromatic hydrocarbons in petroleum fractions, [13]. According to the data of N.D.Zelinsky and N.I.Shuykin, the methyl cyclohexane fraction is enriched with toluene above Zelinsky's catalysts [22].

The formation of aromatic hydrocarbons in petroleum is of technological interest both with regard to the anti-knock properties of gasolines and the production of toluol.

The reaction for forming aromatic hydrocarbons in petroleum was discovered in 1878 by A.A.Leton (Leningrad Technological Institute).

Subsequently different methods of forming aromatic compounds were developed both here and abroad; for example, the thermal re-formation of crude petroleum. The catalytic dehydrogenation of Zelinsky and the formation of aromatic hydrocarbons from paraffins by other Soviet chemists is of interest with regard to the formation of aromatics in petroleum.

In this article, we have been able to touch in only the briefest manner upon the chemistry of hydrocarbons and petroleum. However, what we have already said indicates that a great deal of work has been done in the Soviet Union in this field where questions of theory and practice are so closely interwoven.

2. Diethylene, Vinylacetylene, and Ethylene Hydrocarbons, and Synthetic Rubbers

At the end of the past century, I.L.Kondakov, and in particular A.E.Favorsky and the latter's students – V.A.Mokievsky, N.M.Vittorf, and others – accurately determined [23] the structure of isoprene $CH_2=C(CH_3)-CH=CH_2$, of links of which the molecules of natural rubber were constructed. Russian chemists discovered many facts about the polymerization of divinyl hydrocarbons to give polymers similar to rubber; this greatly added to the information noted by earlier investigators, among them different Russians [24] (V.A.Mokievsky in 1898) with regard to isoprene, which could be polymerized by the action of different agents (temperature, light).

N.N.Mariutsa [25], a student of M.D.Lvov, synthesized diisopropenyl – $CH_2=C(CH_3)-C(CH_3)=CH_2$ – and observed its tendency to polymerize to a viscous product upon heating.

Later (1900) I.L.Kondakov [25], by heating diisopropenyl with alkali to 150°, converted it into a leathery polymer, and then (1902) described its spontaneous conversion into a rubber-like polymer. Earlier (1895) A.M.Berkenheim had polymerized [26] piperylene, $CH_3-CH=CH-CH=CH-CH_3$, by heating it to 250°.

Using these facts, German chemists organized a small-scale production of the synthetic methyl-isoprene rubber of Mariutsa and Kondakov in the imperialist war of 1914 to 1918. Subsequently, S.V.Lebedev greatly increased the number of divinyl hydrocarbons known to be capable of polymerization (1909-1912).

A very important fact, which is fundamental in the modern chemistry of synthetic rubbers and has to do with the thermal polymerization of divinyl, was first noted by S.V.Lebedev and published by him in December, 1909 [27]. The scientific basis for the polymerization of diethylene and other hydrocarbons was contained in a remarkable dissertation for a master's degree by S.V.Lebedev (1913).

The processes of polymerization of saturated hydrocarbons have been successfully studied in the Soviet period by S.V.Lebedev and our other chemists (in latter years, by S.S.Medvedev, B.A.Dogadkin, A.N.Yurzhenko, B.A.Dolgoplosko, and others).

The great requirements of the Soviet State for rubber impelled the supreme Soviet of the People's Economy in January, 1926 to announce a world competition

for the production of synthetic rubber, the materials to be submitted within a period up to January 1, 1928.

S.V.Lebedev, then Professor of the Kirov Military-Medical Academy and of the Chemical Faculty of Leningrad State University, together with his coworkers and teachers of the Kirov Mil.-Med. Academy and his coworkers and students of the University, energetically and diligently devoted himself to solving the problem of producing synthetic rubber.

To obtain divinyl, Lebedev set out at first in two ways: 1) the pyrolysis of petroleum, and 2) the contact decomposition of alcohol to give divinyl. Having become convinced of the complicated nature of the method from petroleum, Lebedev's group began to develop a synthesis from alcohol, which was a practicable raw material, and brilliantly solved the problem.

One of our most noted specialists in the field of rubber (vulcanization) is B.V.Bizov, also a student of A.E.Favorsky. Both in those years and earlier, he carried out experiments on the synthesis of divinyl from petroleum, but because of the complicated nature of the reaction could not obtain favorable results. B.V. Bizov and S.V.Lebedev introduced many new facts into the problem of obtaining divinyl from petroleum.

On December 30, 1927, S.V.Lebedev presented for the competition 2 kilos of sodium-divinyl rubber and a description of his method. Lebedev's method was accepted as extremely valuable, and S.V.Lebedev was awarded the prize. The work of Lebedev and his students was actively continued.

In 1929, the Central Committee of the CPSU (Bolsheviks) had already made a decision to expedite the putting into practice of Lebedev's method. To this end, S.M.Kirov lent every possible assistance. In 1930, a large laboratory was organized and construction of a Type B pilot plant was begun. Toward the end of the year the pilot set-up had already been completed and an experimental sheet of Lebedev's divinyl rubber weighing 250 kilos was quickly obtained.

S.M.Kirov gave many concrete indications of how necessary it was to carry the work further in order to increase the production indexes attained. In 1931, the Government commission of experts approved Lebedev's method, and confirmed its high industrial value. After many efforts, the new rubber was successfully transformed into a high quality finished rubber. A large factory was swiftly constructed and Lebedev's synthetic rubber guaranteed the meeting of the rubber requirements of the Soviet Union.

By a decree of the government on August 7, 1931, S.V.Lebedev was awarded the order of Lenin "for his special service in solving the problem of obtaining synthetic rubber". Upon receiving this high award, S.V.Lebedev pronounced these significant words, which are an expression of the thinking and feeling of Soviet scientists: "The government has decided to convert the success attained by me and my coworkers into the basis for constructing a new branch of industry...There can be not the slightest doubt that only with us, in the country of the building of socialism, is such a great creative range possible. The greatest happiness is to see one's thought converted into a deed of such grandeur."

The great creative work of S.V.Lebedev and his coworkers, and their broad scientific investigations, were introduced into the development of the technological process of production of synthetic divinyl rubber according to Lebedev's method. Production in its turn set a great number of problems before theoretical science, upon whose solution Lebedev's scientific school is now working with success.

The Soviet synthetic divinyl Lebedev rubber industry became the model for other countries. It is known that abroad (USA) the synthetic rubber industry was

developed in the years of the second imperialist war.

The theoretical foundations for obtaining divinyl from alcohol were considered by S.V.Lebedev in his further work in 1933 [28].

It was noted that the reactions for the formation of divinyl, ethylene, and aldehyde from alcohol over a Lebedev catalyst which had dehydrogenating and dehydrating components in its composition were mutually interdependent. S.V.Lebedev found that divinyl was formed not from already prepared molecules of aldehyde and ethylene, but at some phase of the process preceding the final formation of these molecules. The molecules of aldehyde and ethylene are already waste-products of the reaction. According to Lebedev, the entire process can be represented by the formation at first from ethyl alcohol of fragments of two types, as a result of splitting off of water or of a molecule of hydrogen:

$$CH_3-CH_2OH \longrightarrow H_2O^+ - CH_2-CH_2-$$

$$CH_3-CH_2OH \longrightarrow H_2^+ - CH_2-CH(OH)-$$

These fragments can be partially rearranged to give ethylene and acetaldehyde, in a side reaction, or they can lead to more complicated molecules, to form at some further stage divinyl and a series of other products. We must note that at present as distingusihed from the situation that existed in the first years of production of synthetic rubber, few hyproducts are obtained. In an article of ours there is given a detailed scheme showing the formation of the different byproducts.

Lebedev's students made a detailed study of the Lebedev synthesis of divinyl. Many investigations were devoted by Yu.A.Forin [29] to clearing up the manner of formation of divinyl hydrocarbons from alcohol and from its mixtures with aldehydes and ketones.

Great significance was attached in these investigations to the aldol condensation of the aldehyde corresponding to the alcohol, to unsaturated aldehydes, (crotonic), and to unsaturated alcohols. Crotylic alcohols, by splitting off water, form divinyl hydrocarbons.

Lebedev's reaction for obtaining divinyl hydrocarbons can be extended to higher primary and secondary alcohols. Isobutyric alcohol does not form the divinyl hydrocarbon, giving instead isobutylene and isobutyric aldehyde. Diethylene hydrocarbons are not formed from tertiary alcohols. The formation of divinyl from alcohols, according to Lebedev's method, and from mixtures of ethyl alcohol and acetaldehyde (according to the method of Ostromislensky) [30] over aluminum oxide, may possibly take place in analogous ways. The secondary alcohols, either alone or in mixtures with ketones, are converted into divinyl hydrocarbons through products of the phorone condensation of ketones.

M.Ya. Kagan also considers crotonic aldehyde as an intermediate product in the formation of divinyl from alcohol by Lebedev's method [31]. Of course, in considering such schemes we must never lose sight of the extreme complexity of the reaction and the possibility of different methods of formation of the divinyl hydrocarbons.

In the past years there have been many other investigations of all aspects of the study of divinyl compounds; these have significantly increased the wealth of data about unsaturated hydrocarbons gathered by the schools of Butlerov and Favorsky.

A.E.Favorsky and his coworkers have developed an interesting method of synthesis of isoprene on the basis of the old Favorsky reaction for synthesizing acetylene alcohols by the reaction of acetylene hydrocarbons with ketones in the presence of dry powdered potassium hydroxide. Acetone and acetylene give a tertiary acetylenic alcohol, which is then hydrated to a tertiary ethylene alcohol, and the latter,

by splitting off water, gives isoprene:

$$CH_3COCH_3 + KOH + CH \equiv CH \longrightarrow (CH_3)_2COHC \equiv CH \longrightarrow$$

$$\longrightarrow \begin{cases} (CH_3)_2COH-CH=CH_2 \rightarrow CH_2=C(CH_3)-CH=CH_2 \\ CH_2=C(CH_3)-C \equiv CH. \end{cases}$$

Favorsky's method for obtaining isoprene requires as raw materials acetone, acetylene, alkali, and hydrogen [32].

Synthetic isoprene rubber, similar to the natural in containing isoprene residues in the molecule, is of very great interest both for the study of the various properties of the rubbers and for comparison with the properties of natural rubbers.

Ethylene-acetylene hydrocarbons, whose first general mode of synthesis was the splitting off of water from acetylene alcohols according to Favorsky's method, can be utilized to give haloprenes by the addition of hydrogen chloride to the hydrocarbon. Polymerization of the chloroprenes, as in the case of the simplest homolog of vinyl acetylene, gives a chloroprene rubber, which possesses many interesting properties:

$$CH_2=C(CH_3)-C \equiv CH \longrightarrow$$

$$\longrightarrow CH_2=C(CH_3)-CCl=CH_2 \longrightarrow \text{methyl chloroprene rubber.}$$

Interesting acetylene-allene-diene rearrangements of similar chlor derivatives were studied in Favorsky's laboratory by his students, in particular by T.A.Favorskaya, A.I.Zakharova, and I.A.Favorskaya [33].

From vinylacetylene and butadiene there are obtained halogen and other derivatives of butadiene, and their properties have been studied, in particular in relation to polymerization [34] (A.L.Klebansky, A.A.Petrov, and others).

Many very valuable results have been obtained in the Soviet Union in the development of the chemistry of synthetic rubber, and many copolymers have been prepared. The work of A.M.Butlerov, S.V.Lebedev and others formed the basis for for the copolymerization reactions of isobutylene with divinyl, giving the so-called butyl rubber.

S.V.Lebedev foresaw a great variety of possible synthetic rubbers and considered of great value the new properties by which the different representatives of the synthetic rubbers were characterized: "Plant rubbers do not depend on the kind of rubber tree they came from, they are essentially one and the same isoprene rubber... The synthesis of rubbers is a source of infinite variety. Theory sets no limits to their multiplicity." [35].

II. Natural Substances of High Molecular Weight – Proteins and Cellulose

During the past quarter of a century very great interest has arisen in substances of high molecular weight, as a result of their great role in the solutions to many theoretical problems of modern chemistry and physics, and in view of the ever growing extent and variety of their practical significance. Treating of a branch of organic chemistry, the chemistry of substances of high molecular weight has gone far beyond its limits, just as the understanding of the properties of high-molecular weight substances has, and in particular, the dependence upon the very valuable mechanical indexes of composition, structure and size of molecule has been determined only by the fullest possible application of methods using radiant energy and other methods of modern physics and physical chemistry. Characterized by very large molecules, high-molecular weight substances are colloids in themselves (eucolloids) and are capable of forming colloidal solutions under

other than customary conditions. It is therefore not surprising that in colloid chemistry a great deal of attention is given to high-molecular weight substances and that the study of their properties is impossible without a broad application of colloid chemistry.

The great practical problems which must be solved in the utilization of high molecular weight substances, and the correspondingly high level of the general modern development of chemistry and physics have resulted in a profound investigation of large molecules; this has been the reason for the great progress in the chemistry of high-molecular compounds in the Soviet Union and abroad.

An especially broad variety of properties, and a high degree of development of one or another characteristic of materials can be secured with synthetic high-molecular weight compounds. However, the value of such natural materials as protein and starch in particular has also increased tremendously in the past decade, as a result of very great new progress in their practical application and of their importance for an understanding of the nature of high-molecular weight substances. If at the end of the XIXth century it was possible to note only the most general scheme of the structure of polysaccharide and protein molecules, many details of their structure have now become known. Cellulose was and remains the clearest example and the most typical model of a high-molecular weight substance.

However, the success of the synthetic chemistry of high-molecular weight substances, particularly the stormy development of the chemistry of synthetic rubbers, has tremendously extended the range of ideas that have resulted from research on natural high-molecular weight substances.

Synthetic rubbers, from one side, are on the boundary line of synthetic high-molecular weight substances, and on the other, adjoin the natural high-molecular weight substances.

It has been said above in relation to research on the nature of isoprene and other rubber-formers, that in building up the chemistry of synthetic rubbers in Russia, much had been done in the XIXth and early XXth century, but that only in the years of the Stalin Five-Year Plans did there take place a tremendous leap in the development of the foundation of this branch of the chemistry of high-molecular weight compounds; only then did the synthetic rubber industry attain its wide range, the first in the world to do so.

In the other branches of the chemistry of high-molecular weight compounds as well, just as in the general theory of the processes of polymerization, much was accomplished by our chemists even in pre-Revolutionary days; all the same, the chemistry and chemical treatment of cellulose and protein were developed in this country in the pre-Soviet period at a very slow tempo.

The first important example of a polymerized oxygen-containing substance was discovered by A.M.Butlerov in the polymers of formaldehyde (1858-1860). In our own day, the polymers of formaldehyde have been called " model molecules of cellulose".

A.M.Butlerov carried out the condensation of formaldehyde under the influence of lime to give a sugar-like substance; this helped determine the formula of the monoses and laid the basis for the theory of the photosynthesis of starch in the green parts of plants (in the chloroplasts) by means of carbon dioxide and water under the influence of sunlight (at the beginning of the career of the great German chemist Adolf Baeyer in the seventies of the past century).

The most important facts in the chemistry of starch and the polysaccharides – the hydrolysis of starch to give glucose in the presence of sulfuric acid, and to give maltose under the influence of diastase – were discovered by the Petersburg Academician Kirchoff, from 1806 to 1814.

There is no doubt that in the development of the chemistry of synthetic high-polymer substances the work of A.M.Butlerov on the polymerization of ethylene hydrocarbons was of importance, in particular his work on isobutylene (in sulfuric acid and boron fluoride media). In our time, polyisobutylene, polythene, and butyl rubber are valuable high-polymers. From this work there arose the very definite problem of how polymerization took place. We now know that only low-molecular polymers are formed by a stepwise mechanism, whereas high-polymers are formed from monomers by chain reactions.

S.V.Lebedev (1913) arrived at the firm conviction that there was a sharp distinction in the properties and manner of formation of the low (dimers and others) and high polymers. He correctly considered the molecules of rubber as a variety of large chain molecules, while the well-known German chemist Harries and others maintained the opinion (until the end of the twenties) that rubber and other high-molecular weight substances containing molecules of high polymers, were small ring-shaped structures, with a tendency to associate to give large aggregates because of supplementary valences or van der Waals forces.

During the past 20 years, investigators have solved many questions of principle in the chemistry of high-molecular compounds. We have already mentioned above the explanation of the mechanism of polymerization processes (S.S. Medvedev and others) and of polycondensation (A.A.Vansheidt, V.V.Korshak, S.R. Rafikov, Z.A.Rogovin and others).

High-molecular substances are being investigated [36] with roentgen rays, cathode rays, and the polarization microscope. Great successes have been achieved in the study of the mechanical properties of high polymers possessing great stability and a high degree of elasticity (A.P.Alexandrov, P.P.Kobeko, V.A. Kargin, P.V.Kozlov, and others).

The work of Soviet scientists has shown that the mechanical properties of high polymers may be regarded from a single point of view [37]. High polymers show a very sharply expressed relaxation phenomenon (return to equilibrium after deformation); the different kinds of behavior upon deformation of the different groups of high polymers are explained by the difference in the velocity of their relaxation.

Many complicated questions concerning the properties of solutions of high-polymeric substances, and the relationships of the latter to solvents, their viscosity, etc., have been elucidated in the work of our chemists (I.I.Zhukov, A.V.Dumansky, S.M.Lipatov, V.A.Kargin, A.G.Pasinsky, S.A.Glikman, Z.A.Rogovin, and many others), but this goes beyond the range of our article.

1. The Chemistry of Proteins

There is no need to dwell on the great role of proteins in living processes. Engels had already said, "Everywhere where there is life, we find that it is related to a protein body, and everywhere where there is a protein body not in the process of decomposition, we also find, without exception, the phenomenon of life". It is therefore not surprising that the chemistry of proteins has always attracted the particular attention of biochemists, physiologists, and nutritionists. At the same time, proteins are an important source of raw material for the chemical industry and for the most important organic substances, a knowledge of whose nature has developed in relation to the successes of chemistry, and in turn exercises an influence on the development of the chemistry of high-molecular weight substances.

It is necessary to point out that in the past quarter of a century our scientific and technical interest in proteins has increased tremendously, inspiring a number of works which have clarified the composition and structure of protein molecules.

Even in the XIXth century, research on the hydrolytic cleavage of proteins showed that the chief product of this process consisted of amino acids, and in addition, of small quantities of the anhydrous forms of amino acids – the diketopiperazines, which were easily formed from amino acids, and the dipeptides, which were without difficulty converted in alkaline medium into salts of amino acids. N.D.Zelinsky in 1914 expressed his belief in the role of the diketopiperazines in the structure of protein molecules [38].

Applying improved methods of hydrolysis of proteins, N.D.Zelinsky in collaboration with V.S.Sadikov (from 1923 on) and N.I.Garilov (from 1927 on) reached the conviction that diketopiperazines were stable and in addition were primary products of the hydrolysis of proteins on a par with amino acids.

The isolation of the anhydride form preexisting in the protein molecule, depends, in N.D.Zelinsky's opinion, on the conditions of hydrolysis; for example, autoclave hydrolysis with 25% formic acid and 4 – * % mineral acid results in complete splitting of the diketopiperazine structural element [39].

In the work of N.D.Zelinsky and V.S.Sadikov in 1923, they expressed a diketopiperazine theory of the protein molecule. The German biochemist, Abderhalden, quickly adopted this theory.

In the twenties, the diketopiperazine theory was received with sympathy by those who believed that high-molecular weight substances possessed small ring molecules with a tendency to associate because of residual valences into large aggregates, and to give colloidal solutions (association colloids). Examples of such small ring molecules with a tendency to associate to form complexes were supposed to be cellulose — (by Hess, Pringsheim, and Karrer) and rubber (by Harries and others).

The theory of associated complexes for high-molecular weight compounds was abandoned by its supporters in the thirties on every front of the chemistry of high-molecular weight compounds, which were not taken to be eucolloids. Protein was regarded as having a polypeptide structure, a view which had been particularly defended earlier by Emil Fischer (1899-1919). The diketopiperazine theory of the structure of proteins was further developed in the work of various authors and interpreted by them in a way that was unacceptable to N.D.Zelinsky and N.I.Gavrilov.

We shall leave to one side the other theories of the structure of protein, for instance that of Trezengard (pyrrole rings), which later became the piperazine theory of protein structure, Bergmann's theory (oxazpline rings), Karrer's imidazoline units), etc.

Accepting the tautomeric forms of diketopiperazines with multiple bonds, which made it possible to write down polymers in the form of condensed rings, the English mathematician Wrinch developed a singular cyclic theory of the structure of proteins, not based upon experiment, in which diketopiperazines formed triazine cycles with a peculiar macrocyclic structure. The theory was at one time accepted by D.L.Talmud [40].

However, the formula proposed by Wrinch was contradicted by a number of facts (the fact that triazine rings had not been shown present, the abundance of double bonds, of enolic hydroxyl, etc.).

A complicated and unstable structure of the protein molecule was proposed by M.S.Renichenko [41] (easy closing and opening of the rings, the presence of polypeptide and ring-shaped links).

N.I.Gavrilov and his coworkers, in a number of investigations showed the presence in proteins of cyclic units, along with peptide structures, and thus revealed the amide linkage in proteins.

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*illegible numeral.

The demonstration of diketopiperazine in native unaltered protein was made by different methods.

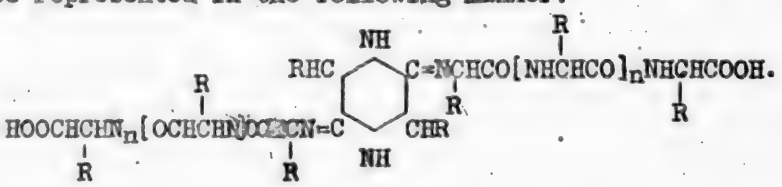
An ionophoretic method permitted the separation of amino acids and peptides from the diketopiperazines [42]. In order to eliminate the possible suspicion that in the application of this method the diketopiperazines might be formed at the moment of destruction, a method for the electrolytic reduction of the diketopiperazines in unchanged protein was used. The experiment showed that in the process, the NHCO grouping was not reduced to peptides, but that the ring units were reduced quantitatively [43].

It thus became possible to determine the number of piperazine rings in native protein. Model amidine structures of piperazine and amino acids [44] were synthesized, and it was shown that their ability to be fermented by enzymic systems of pepsin and stomach juice was due [45] to a specific enzyme, "amidinase", which hydrolyzed amidine groups existing in native protein.

It was shown that protein contained along with the amidine structure short polypeptide chains (tripeptide chains); this was discovered from research on the absorption spectra of copper peptide complexes [46].

The discovery of the amidine group in proteins was an important factor.

The researches of N.D.Zelinsky, N.I.Gavrilov, and their coworkers cleared up many things about the structure of the protein molecule. The protein micromolecule can be represented in the following manner:



Of course, every different kind of protein will have its own structure. It is probable that in several converted (denatured) proteins the three-dimensional structures which are very frequently met in the group of high-polymers (bakelite, ethyl cellulose, etc.) also play a role.

The synthesis of protein is of great interest. It is known that the synthesis of polypeptides is to some extent an approach to the synthesis of protein. Our well-known biochemist Danilevsky [47] had long before described the synthesizing action of pepsin on protein hydrolysates. He had obtained preparations known as plasteins, but with properties very much altered from those of the protein before hydrolysis.

Experiments by different investigators showed that pressure favorably influenced polymerization and condensation.

These two factors, enzymic action and pressure, were successfully utilized in the work of S.E.Bresler and his coworkers [48]. Protein was first hydrolyzed by an enzyme in a buffered medium. The hydrolysate obtained was then subjected in a special apparatus, to a pressure of 5 to 6 thousand atmospheres at 37°; during this process, the reverse synthesis of polypeptide rings took place. The experiments were carried out with a number of protein hydrolysates. Sufficiently satisfactory data were obtained to confirm the fact that the synthesis of protein molecules actually took place as a result of the reversibility of the enzymic action and the important role of the pressure.

The quasiproteins obtained differed from Danilevsky's plasteins in being similar to the original proteins.

It was shown that in an aqueous solution under a pressure of 5,000 atmospheres, it was possible to synthesize from a tripeptide ester (trialanine) a polypeptide containing 12 to 13 amino acid residues [49].

During the past years protein has found various forms of technical application. For example, a method has been developed for producing not only milk casein but plant casein (Byelorussian Academy of Sciences, Lenin Agricultural Academy), for utilization in the manufacture of fibers and plastic; in this article, however, we shall disregard these developments as having comparatively narrow technical value.

In the past 25 years, a great many investigations have been devoted in this country to the chemistry of protein, and great progress has been made in the USSR in this branch of the chemistry of high molecular weight compounds.

2. Most Important Progress in the Chemistry of Carbohydrates

The great biological, nutritional, and technological importance of carbohydrates is the reason for their extensive production and for the great scientific interest in this group of substances. Sucrose has firmly established itself in our lives as a useful nutritional substance. The extraction of sucrose from sugar beets has become a gigantic industry in the USSR. Here there is a close relation between agronomy, Michurian science, and chemistry.

The products of hydrolysis of wood are an enormous resource of carbohydrates; a partial alkali sulfite treatment gives a mixture of monoses. These are hexoses which can be fermented to give ethyl alcohol, suitable for transformation into divinyl according to Lebedev's process. Thus the forestry and cellulose industries come to the aid of the industry for manufacturing the Lebedev divinyl synthetic rubber. Many branches of industry have been built upon starch and especially upon cellulose raw material. Its great storehouse in nature, renewed every year, and its extremely remarkable physico-chemical, physico-mechanical and chemical properties make cellulose a most valuable material for paper, for cotton fabrics, and for chemical transformation into artificial fibers, motion picture film, and plastics.

Earlier, in pre-Revolutionary Russia, a small group of technological paper manufacturers and textile manufacturers was interested in cellulose. Only isolated representatives of chemical technology, like A.M.Nastyukov and A.V.Sapozhnikov, carried out any significant investigations in this field.

The situation was basically changed in Soviet times, when a large number of scientific personnel were trained to study cellulose and its derivatives, in connection with different branches of industry. There was rapid development in the years of the Stalin Five-Year Plan (artificial fiber, moving picture film, celluloid, etc.) The scientific workers in the fields of physical and colloid chemistry and in physics successfully began to carry out research on cellulose products.

In the modern progress of the chemistry of cellulose, a great role has been played by the brilliant development of the chemistry of the simpler sugars at the end of the past century, and particularly in the twenties of the present century. In the Soviet Union during the past 25 years there has been developed with considerable originality, particularly by Favorsky's school, the chemistry of monohydroxylic aldehydes and ketones (hydroxycarbonyl compounds); these represent the simplest models of sugars, and the chemistry of monoses and disaccharides.

The Characteristic Reactions of the Simplest Hydroxycarbonyl Compounds and Monoses. A.E.Favorsky [50] found that unsymmetrical dichloroketones could be obtained

from acetylene hydrocarbons by the action of hypochlorous acid; he then discovered that these could be transformed, by a spontaneous oxidation-reduction reaction, into an acid of the ethylene series (1895) and was able to pass from mono-halogenated ketones to hydroxy-ketones and to definite acids (1913-1928). Favorsky united in his work the synthetic transformation of acetylene hydrocarbons and hydroxy-carbonyl compounds. Interesting intramolecular oxidation-reduction reactions were found (1928) to transform hydroxy ketones into isomeric hydroxyketones [51], the alcoholic and ketonic groups changing places in such a way that the ketone group moved toward the end of the chain (A.E.Favorsky, A.I.Umnova, V.N.Vasilyev, E.D. Venus-Danilova, and others).

S.N.Danilov and E.D.Venus-Danilova (1919-1938) came even closer to the models of the transformations in carbohydrates. They studied in the hydroxyaldehydes the oxidation-reduction transformations that were typical of sugars.

The most important intramolecular oxidation-reduction transformations of sugars are represented by the reciprocal epimeric changes of aldose and ketose, and the rearrangements of the monoses to give other sugars, discovered in the last quarter of the XIXth century. These two types of transformation of sugars similar to the well-known Cannizzaro reaction of the transformation of aldehydes into alcohol and acid, are at the basis of many biochemical changes, for example, of the alcoholic and other fermentations of sugars. The epimeric conversion of monoses was discovered by Lobry de Bruyn (1895), definitely in relation to the study of the synthesis of sugars made by Butlerov, who subjected formaldehyde to the action of lime, and obtained a mixture of monoses, with a predominance of ketoses instead of aldoses.

We may note that the use of organic bases (pyridine, quinoline) favors the epimeric conversion of monoses [52]. As a result of the action of lime on cellobiose, S.N.Danilov and P.T.Pastukhov obtained [53] β-(1,5)-glucosido-4-(1.5)-mannose, and, apparently, ketocellobiose.

To explain the epimerization of sugars, Lobry de Bruyn made use of an alcoholic hydroxyl scheme which had first been used by Butlerov in the formula of his oxoketenol:

$$(CH_3)_3C \cdot COH \begin{array}{l} \diagup \\ \diagdown \end{array} \begin{array}{l} CH(CH_3)_2 \\ O \end{array}$$

obtained from a dimer of isobutylene.

Somewhat earlier, chlorhydroxyl and alcoholic hydroxyl structures had been applied to a great extent by A.E.Favorsky to explain the transformation of dichloroketones into acrylic acids (1894-1895) and of chloroketones of the polymethylene series into polymethylene acids [54] (1913-1918); later (1928) Favorsky used this scheme to explain alcoholic fermentation and the transformation of ketoalcohols into isomeric ketoalcohols. All these reactions, discovered by A.E.Favorsky and developed by him and his students, were of an interest that far surpassed the boundaries of the field of molecular rearrangement of organic compounds. The isomeric transformations of ketoalcohols were studied in detail by A.E.Favorsky in the twenties. This field of isomeric transformations of ketoalcohols has been developed during the past years by A.F.Khaletsky [55] and is being investigated at present by T.I.Temnikova [56].

Priority in the development of the reaction for isomeric transformations of ketones (first published by Favorsky in 1914), which began to attract attention abroad in the twenties and thirties, belongs to the school of Favorsky.

Closely related to these investigations of Favorsky, and actually an extension of them, is the work of S.N.Danilov and E.D.Venus-Danilova on the isomeric

transformations of aldehydes and hydroxyaldehyde compounds.

In 1919, S.N.Danilov described in detail the ketone rearrangement of aldehydes, and remarked on the great significance of this rearrangement in the transformations of α-glycols when water was eliminated from them. Later, from 1925 on, in collaboration with E.D.Venus-Danilova, he extended this reaction to a number of aldehydes with open chains. The ketone transformation of aldehydes has also been investigated abroad (from 1926 on).

The isomeric transformation of ketones into other ketones which had been expected (by S.N.Danilov) was discovered by the investigations of A.E. Favorsky and A.A.Chilingaryan (1926), and developed in a number of later investigations. During the past few years it has been investigated in detail by T.E.Zalesska [57].

The ketone transformation of aldehyde structures was extended by S.N.Danilov [58] (from 1927 on) to α-hydroxyaldehydes and developed in collaboration with E.D.Venus-Danilova for a number of α-hydroxyaldehydes. It was shown that not only the halogenated aldehydes, but the α-hydroxyaldehydes with tertiary alcoholic groups were themselves capable of undergoing transformation into acid in the presence of the appropriate reagents. In a large number of investigations, E.D. Venus-Danilova [59] described the ketone transformation of aldehydes, as well as the hydroxy-ketone and acid transformations of α-hydroxyaldehydes of the polymethylene series. She observed interesting cases of widening, narrowing and opening of polymethylene rings (1938), similar to the transformations of rings in polymethylene hydrocarbons and alcohols discovered by our chemists (N.M.Kizhner, N.Ya. Demyanov).

Like the α-halogenaldehydes, the 2-halogen monoses isomerize under the action of lead hydroxide to give sugar acids of a new type (desone acids); these have been obtained by S.N.Danilov and A.M.Gakhokidze from monoses, and in the very last few years by A.M.Gakhokidze from a number of bioses [60].

Our chemists (A.M.Kuzin, S.A.Balezin) have introduced essential new features into our concepts of the old Butlerov reaction on the synthesis of monoses from formaldehyde.

Kuzin's investigations [61] have shown the autocatalytic nature of Butlerov's reaction, the catalytic role being ascribed to the enediol forms of the sugars. Using a dilatometric method to study this reaction, Balezin [62] has arrived at the conclusion that lime is a component part of the intermediate complex of the initiating centers and that its role is not limited to the creation of a definite alkalinity of the medium.

While speaking of the synthesis of sugars, we must note that A.M.Gakhokidze [63] has successfully synthesized bioses with connecting links in other than the usual positions; these are encountered in nature in the disaccharides, with links particularly in the 1,3 positions (glucosido-3-glucose), and he has suggested methods for finding the positions of linkage.

Sugar rearrangements, including diastereoisomeric rearrangements of the monoses and disaccharides, are of direct interest in the chemistry of cellulose. We may assume that in alkaline media the cellulose molecules are capable not only of being oxidized or split by hydrolysis, but also of undergoing diastereoisomeric and epimeric transformations and a sugar rearrarangement; the same thing would be especially true of the products of hydrolysis of cellulose. In alkali cellulose which has undergone long aging, sugar acids are actually found (A.S. Shpitalni [64]).

We have achieved great success in the hydrolysis of wood under industrial conditions (Sharkov, Chepigo, Martinenko, Ivanov). Wood hydrolysis is of great

interest because of the fact that it is a means of preparing large quantities of monoses, which are a valuable material for the production of alcohol and for other requirements [65].

The acetolysis of cellulose, in which cellulose gives a cellobiose octa-acetate, has been studied in detail by S.N.Danilov and P.T.Pastukhov, who have developed the optimal conditions for the reaction, in particular with regard to the choice of a catalyst, and have studied the velocity of the reaction [66]. The acetolysis of cellulose is regarded as a solvolytic oxidation-reduction reaction.

Cellulose Fibers. In connection with the hydrolytic and acetolytic splitting of cellulose, attention has been drawn to hydrocellulose, which is in the form of a cellulose fiber that has undergone acid treatment; during the treatment, the cellulose has undergone swelling, and possibly, to some degree, hydrolysis.

The weakest indications of hydrolysis occur during the swelling of cellulose in phosphoric acid. At the proper concentration of solution, there are obtained, after removal of the acid, mechanically stable masses of cellulose, in porous form, (S.N.Danilov, N.F.Gintse [67]).

Preparations of cellulose which have undergone alkaline treatment, so-called cellulose hydrate, have been studied under various conditions; artificial fibers and films, made by the viscose and copper-ammonium methods, are cellulose hydrate. The investigations of both cellulose hydrate and the natural fibers are of interest with regard to cellulose structure.

The methods of roentgenographic investigation and of electronographic study by the diffraction of rapid electrons have been applied to fibers in the USSR; these have shown that cellulose fibers do not possess a microcrystalline structure. In the investigations of nitrocellulose films by the method of diffraction of rapid electrons, V.A.Kargin, back in 1937, arrived at the conclusion that the width of the zones of interference on the electronogram were the same as for the roentgenogram, and that this proved the amorphous nature of the cellulose esters, and the absence of microcrystalline complication.

The same fact was confirmed [69] for cellulose hydrate film (cellophane) which had undergone stretching, by the work of Kargin and Leypunska on the diffraction of different wave lengths – from 0.06 Å (rapid electrons) to 1.54 Å (X-rays).

Upon stretching of the film, the diffraction pattern on the roentgenogram was changed (emergence of texture) but the electronogram showed no change; consequently, there was no regularity in the distribution of the macromolecules.

The formation of roentgenograms, like the double refraction of cellulose fibers, does not testify to the crystalline nature of fibers, as parallel roentgenographic and electronographic determinations do not confirm it. The presence of double refraction indicates only a suitable distribution of macromolecules in the fiber [70].

V.A.Kargin and N.V.Mikhailov, in a number of works, have studied the question of orientation of macromolecules in natural fibers and in cellulose hydrate, and of changes of orientation under the influence of different reagents (tensile stress, heating in liquids [71]) both of these in relation to mechanical properties which are of interest for the production of artificial cellulose fibers.

The work of our chemists has led to the new conclusion that cellulose has an amorphous structure and that there is actually a single phase system in cellulose fiber; this means that there are no phase changes during the action of different reagents upon cellulose.

Cotton and wood cellulose, the latter containing chiefly sulfite cellulose,

are suitable materials for chemical utilization. Beginning at the end of the twenties, we have begun to use large-scale mechanical devices for the complete purification of cotton cellulose and for obtaining high quality sulfite cellulose [72], guaranteeing the production of high quality viscose fibers and films.

We now have at our disposal large quantities of high-quality cotton cellulose and highly improved wood cellulose for the artificial fiber industry, for motion picture films, and for plastics.

Chemical Transformation of Cellulose. Large quantities of technical cellulose are transformed into artificial viscose silk, artificial wool, cord for automobile tire casings, and viscose film (cellophane), and also by means of the cuprammonium process into artificial silk and artificial wool. The chemical operations serve only to put the cellulose into solution in the form of cellulose xanthogenates of cuprammonium complexes, and then the cellulose is regenerated again in the free form, in the shape of a fiber or film.

By their own skills our specialists have developed very successful technological processes for the production of both forms of artificial cellulose fiber; the literature, both in the form of journal articles and of monographs, is broad and very inclusive; in it are published many significant facts concerning the chemistry of cellulose and high-molecular weight compounds. We may say that durint the Stalin Five-Year Plans there has been constructed a new, previously nonexistent industry for the chemical transformation of cellulose, and that numerous scientific and technical personnel have been supplied, greatly increasing the number of investigators in this field.

O.P.Golova and V.I.Ivanov [73], working with cuprammonium solutions of cellulose, have made the interesting observation that the long-known fact that the viscosity of cellulose in cuprammonium solutions is lowered upon the addition of air must have far more significance than is generally supposed. Therefore, in determining the viscosity and molecular weights of celluloses in these solutions, even a very small quantity of air considerably lowers the viscosity and molecular weight (they recommend a vacuum of 10^{-6} mm.)

S.N.Danilov and his coworkers (1937-1940) [74], have investigated the basic salts of copper and the influence of electrolytes on the viscosity of cuprammonium solutions. According to their experiments, sodium sulfite and thiosulfate, and to some extent, added organic substances, strongly inhibit the oxidation of cellulose and ammonia in cuprammonium solutions; the organic substances added increase the stability of the copper tetrammonium complex. A.V.Pakshver and M.I.Arkipov [75] have investigated the solubility of copper hydroxide in ammonia, and have determined the composition of complexes; they have also studied other problems of the chemistry of cuprammonium solutions used for the spinning of fibers.

There are many more investigations of the chemistry of the xanthogenates and of viscose, which are closely related to the practical problems of the viscose industry; in a short period, we have achieved a high level of technical development.

N.N.Nikitin [78] has studied the influence of refrigeration upon the swelling of cellulose in alkali and has found that the swelling is greatly increased, in accordance with definite rules relating the swelling of cellulose to the degree of lowering of the temperature. He has noted the significance in this process of a decrease in the viscosity of the cellulose, of an increase in the tendency to hydrolyze, and of the hygroscopicity. In this connection, we may point out that these authors have also investigated the production of soluble xanthogenates with a small expenditure of carbon disulfide at low temperatures. Z.A Rogovin has also studied the influence of different factors on the properties of cellulose xanthogenates [77].

The action of the oxygen of the air tends (S.N.Danilov and others) to form dixanthogenides and polysulfide compounds in viscose, influencing the course of its ripening. Potassium cyanide may serve as a reagent for the various polysulfide compounds in viscose, capable of removing the sulfur from disulfide compounds, in a manner similar to that of sodium sulfite and arsenite. Thus, an important role is played in viscose by hydrolytic processes taking place simultaneously with oxidation-reduction, oxidizing and anti-oxidizing processes, and the interchange of sulfur atoms of polysulfide compounds with other compounds. (S.N.Danilov, O.P. Kozmina, N.M.Grad, and others [78]).

Broad scientific investigations and particular branches of chemical industry are bound up with the esters and ethers of cellulose. We may name nitrocellulose as ranking first in importance. In the work of D.I.Mendelyeev, who discovered pyrocolloids, of A.V.Sapozhnikov, who gave the first theory of the nitration of cellulose and had a correct concept of nitrocellulose, as well as of high-molecular weight substances of heterogeneous composition, and in a number of other investigations, Russian science has contributed much to this chapter of the chemistry and chemical transformation of cellulose. At present, all aspects of the cellulose esters are being studied, a fact which is not surprising, as extremely important industries are based upon nitrocellulose.

Sapozhnikov's theory of the nitration of cellulose has been extended in the work of Danilov, Matveyev, and Buchhalter on mixtures of phosphoric and nitric acids; here the swelling of cellulose in the nitrating mixture [79] plays an important role.

There is a very extensive literature on the relationships between nitrocellulose and solvents. For example, the energy of this relationship is greatly dependent upon the degree of nitration and upon the nature of the solvent, characterized by its swelling pressure [80] (Danilov, Dinkin).

The synthesis and investigation of the properties of cellulose ethers have been carried out over a period of years in different works by the laboratories of P.P. Shorygin, S.N.Ushakov, N.I.Nikitin, S.N.Danilov, and others, who have introduced important aspects into the treatment of this group of substances [81].

Interesting examples of high-molecular weight tri-dimensional structures are described in a number of works, particularly with regard to the esters and ethers of cellulose. For example, the properties of cellulose glycerine ethers, of allylcellulose, and of others [82] have received special study in this regard.

As in this short sketch it is impossible to consider even the most important facts in the chemistry of cellulose that have been discovered by Soviet scientists, we shall limit ourselves to what has been said, as to some degree illustrating the directions and the great progress of Soviet science in the chemistry of high-molecular weight compounds.

The brief data given above on the progress of Soviet chemistry in the years of the Stalin Five-Year Plans are sufficient to indicate the characteristic features of our science.

We may say with pride that Soviet chemists devote all their energy to what is, to large numbers of its representatives, "that science which does not depart from the people, does not hold itself separate from the people, but is prepared to serve the people, prepared to give to the people all the achievements of science, which serves the people not because of compulsion, but willingly, of its own desire" (J.V.Stalin).

The great successes of Soviet chemical science are due to Stalin, the coryphaeus of science, the teacher and guide of the peoples of the USSR, the leader and organizer of the gigantic victories of our state in industry, agriculture, science, and general culture.

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REFRACTOMETRIC DATA ON HIGHER MOLECULAR COMPOUNDS IN SOLUTIONS OF MIXED SALTS

N. F. Ermolenko and S. Ya. Levitman

Between typical compounds of the first order and those of higher orders, there are, as is well known, intermediate forms, the degree of whose closeness to one order or the other may be characterized by the stability of the form or the dissociation constant of its complex ions.

The less stable the given compound of a higher order, the greater is the dissociation constant of the complex ion, and the higher the concentration that will be needed for its formation.

This is especially true of the salts of untypical complex-formers, which at low concentrations are regarded as atomic compounds of the first order, while at higher concentrations they are capable of giving compounds of a higher order.

We encounter the question of whether it is possible to form compounds of higher order in salt mixtures when attempts are made to explain the antagonism of ions during the coagulation of sols by mixtures of electrolytes.

In this respect, the mixtures of alkaline metal and magnesium salts, as well as a number of others, are of special interest.

In the present case, we studied the possibility of formation of compounds of higher order in the following systems:

1) $KCl - LiCl - H_2O$,

2) $MgCl_2 - KCl - H_2O$,

3) $SrBr_2 - NH_4Cl - H_2O$,

4) $BaCl_2 - KCl - H_2O$.

To decide whether it was possible to form compounds of a higher order in solutions of salt mixtures, we utilized data on the measurement of melting point depression [1], heat of mixing [2], electrical conductivity, electro-motive forces, etc., and on the basis of the deviations observed from the magnitudes theoretically expected, we decided whether chemical compounds were formed in the mixture.

N.S.Kurnakov's method of physico-chemical analysis showed itself to be especially useful in attaining the purpose indicated. As is known, from the point of view of physico-chemical analysis, a mixture of two salt solutions may be regarded as a three-component system (Salt A, Salt B, and water), and may be represented as a triangle (Fig. 1).

Cuts across the triangle, parallel to side AB, represent a mixture of solutions of substances A and B in various proportions, with constant total concentration. The closer the cut is to the base of the triangle, the greater the total concentration of material.

A series of such cuts, joined to the triangle, gives a complete picture of the relationship of these three substances. To obtain such a cut (AB) a series of mixtures is made up of two equimolecular solutions of both components.

The solutions must contain the same molar percentages of the corresponding salts. Mixtures are made up in such a manner that the sum of the number of moles of both salts in every mixture always remains constant. The composition of the mixtures is given along the axis of abscissas (Fig. 2).

If, now, any physico-chemical property of these mixtures is measured (electrical conductivity, light absorption, viscosity, index of refraction, etc.) and compared with the values of this property calculated from the rule of additivity, the deviation from additivity indicates the existence of a chemical compound between the components, and a maximum or minimum (depending on the course of the curve of deviation with a constant number of moles of the two salts) corresponds to the composition of the compound formed.

If the maximum is formed at the ratio 1:1, the compound obviously has the formula AB; if there is a maximum at the ratio 1:2, the compound is AB_2; with a ratio 2:1, A_2B.

One of the most important methods for determining compounds of a higher order in salt mixtures is the measurement of the index of refraction of the system, and a determination of the deviation of this index from additivity.

A. Glazunov [3] was the first to apply the determination of the index of refraction as a method of physico-chemical analysis. He studied a number of systems, and gave the first classification of isotherms of the index of refraction for binary liquid systems.

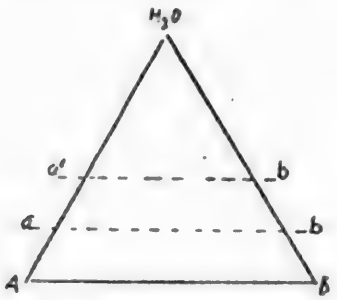

Fig. 1

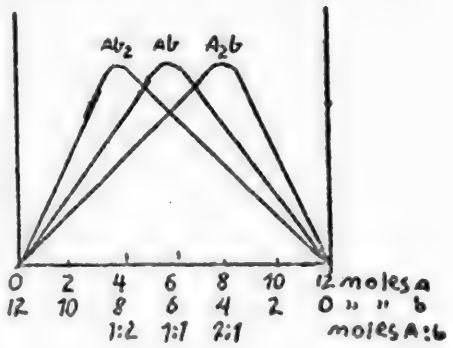

Fig. 2

In a number of works, V. Va. Anusov [4] investigated the change in the index of refraction in a series of liquid systems, and proposed several other classifications.

N.A.Trifonov and G K.Alexandrov [5] carried out a great number of investigations on isotherms of the index of refraction of binary liquid systems.

O.M.Morguleva [6] studied a series of ideal binary systems, such as chlorobenzene—bromobenzene, m-xylene—o-xylene, and showed that the isotherm of the index of refraction of these systems were straight lines or very close to such lines.

N.A.Pushin and P.G.Matavuli [5] investigated a number of systems formed from piperidine and phenols, and also systems formed by acetic acid and amines [7]. In these systems, they observed a deviation of the value of the index of refraction from additivity, the maximum value of these deviations corresponding to a concentration very close to that which represented a chemical compound.

By means of the data on index of refraction of the system $CH_3COOH - H_2O$, we have studied the formation of hydrates of acetic acid [8].

Spaku and Popper [9] studied the formation of compounds of higher order by means of the change of index of refraction in mixtures of salts, using for their calculations the so-called method of continuous variation of Job [10], which was actually a partial case of physico-chemical analysis of a three-component system developed by the school of N.S.Kurnakov.

In the present work, we have studied the already-indicated ternary systems by the method of physico-chemical analysis (using the index of refraction), in order to determine the possibility of formation in aqueous solutions of the given salt mixtures of compounds of higher order, and to determine the composition of these compounds.

For the theoretical calculation of the index of refraction of the mixture ($n_{theoretical}$) starting with the rule of additivity, we utilize the customary formula:

$$\frac{\alpha \cdot n_\alpha + \beta}{\alpha + \beta} = n_{theoret.},$$

where α is the weight (in g) of the initial solution of one salt,
n_α the index of refraction of this initial solution,
β is the weight (in g) of the initial solution of the second salt,
n_β is the index of refraction of the initial solution of the second salt.

Having assumed that in the absence of any chemical reaction the index of refraction of the mixture is the additive value, every deviation observed between the experimentally measured values and the values of the index of refraction calculated by the rule of additivity, are considered due to the formation of a new compound (of higher order) in the solution.

The composition of the compound thus formed is determined from the graph (Fig. 2).

EXPERIMENTAL

All the measurements of the index of refraction were carried out by means of a Pulfrich immersion refractometer. With careful work, the variation of the different readings amounted to $\pm$ 1.82 divisions of the scale, which corresponded to $\pm$ 0.05 units in the fifth decimal place of the index of refraction.

The entire range of the index of refraction necessary for investigating the solutions and mixtures was determined with the aid of three interchangeable prisms, overlapping the following intervals of the index of refraction:

prism 1 n_D from 1.3254 to 1.3664,

prism L-2 n_D from 1.3642 to 1.3999,

prism L-3 n_D from 1.3989 to 1.4360.

The apparatus was carefully adjusted after each change of prism. A test of prism 1 was performed with distilled water, of prisms L-2 and L-3 with special disks.

During the period of measurement, the temperature was kept constant at 20°C ± 0.02°, by means of an ultrathermostat.

To avoid evaporation, all the small vessels containing the solutions while in the Pulfrich apparatus, were covered with rubber stoppers, and the immersion prism was provided with a rubber jar, the vessel being kept covered during the time of making the measurement.

The water for the preparation of the solution required two distillations.

The reagents used were chemically pure (guaranteed) or Pure for Analysis.

The solutions were prepared by dissolving a weighed amount of the material in a weighed quantity of water.

After preparation of the initial solutions, the amount of substances in them was controlled by means of gravimetric titration.

The mixtures were prepared by addition to the previously calculated and weighed amount of solution of the second component calculated and weighed amount of solution of the second component.

Knowing the weight of sample and the indices of refraction of both initial solutions, it was possible to calculate $n_{theoret.}$ from the formula

$$\frac{\alpha \cdot n_\alpha + \beta \cdot n_\beta}{\alpha + \beta} = n_{theoret.}$$

After determining $n_{expt.}$ for each mixture, it was possible to calculate the difference

$$\Delta n = n_{theoret.} - n_{expt.}$$

By marking off along the axis of abscissas the composition of the mixtures investigated and along the ordinate axis the values of the deviation of the index of refraction from additivity (Δ n) it was possible to make a graphic determination of a maximum or minimum in the deviation, and thus to decide whether a compound of a higher order was present in solution.

Below are the numerical data for the systems studied.

System LiCl – NaCl – H_2O

Table 1
Original Solutions

Name	Concentration (in mole %)	$n_D^{20°}$
LiCl.....	4.8732	1.355844
NaCl.....	5.0316	1.358662

Evaluation of Results

In the system LiCl – NaCl – H_2O (Tables 1 and 2, Fig. 3) the deviations of the values of the refractive index from additivity are very insignificant, random, and close to the values that might be due to experimental error. This permits us to draw the conclusion that no compound of higher order is formed in this system.

In the system $MgCl_2$ – KCl – H_2O (Tables 3 and 4, Fig. 4), the deviations of the value of the refractive index are not great, but have a clearly expressed character. The maximum of the deviations is at the ratio $MgCl_2$:KCl = 1, which permits us to assume that the compound $[MgCl_3]K$ is formed in this system.

The sloping character of the deviation curve shows that under the given conditions of concentration and temperature, this compound (of the carnaline type) possesses no great stability.

In the System $BaCl_2$ – KCl – H_2O (Tables 7 and 8, Fig. 5), the deviations of the values of the refractive index from additivity are quite large, reaching 3 units in the fourth decimal place.

Table 2

Mixtures of LiCl and NaCl Solutions

No. of mixture	Grams of original solution		Mole %		$n^{20}_{expt.}$	$n^{20}_{theoret.}$	$\Delta n \cdot 10^6$
	LiCl	NaCl	LiCl	NaCl			
1	3.0188	17.0008	0.7721	4.2444	1.358248	1.358237	11
2	5.0185	15.0618	1.2579	3.7329	1.357960	1.357957	3
3	7.0272	13.0639	1.7524	3.2218	1.357708	1.357676	32
4	8.0287	12.0379	2.0001	2.9663	1.357564	1.357534	30
5	9.0782	11.0194	2.2538	2.7047	1.357420	1.357389	49
6	9.9630	10.0377	2.4799	2.4711	2.357294	1.357258	36
7	11.0039	9.0722	2.7227	2.2205	1.357132	1.357117	15
8	12.0150	8.0050	2.9750	1.9602	1.357006	1.356971	35
9	15.0537	5.0356	3.6907	1.2212	1.356557	1.356550	7

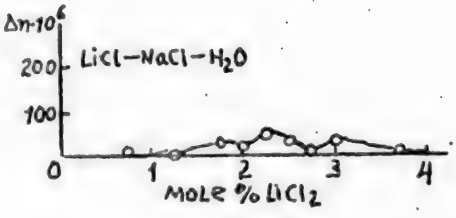

Fig. 3

System $MgCl_2$ – KCl – H_2O

Table 3

Original Solutions

Name	Concentration (in mole %)	n^{20}_D
$MgCl_2$	5.0083	1.392116
KCl	5.0088	1.359346

Table 4

Mixtures of $MgCl_2$ and KCl Solutions

No. of mixture	Grams of original solution		Mole %		$n^{20}_{expt.}$	$n^{20}_{theoret}$	$\Delta n \cdot 10^6$
	$MgCl_2$	KCl	$MgCl_2$	KCl			
1	3.4420	16.3780	0.8340	4.1700	1.365025	1.365037	−12
2	5.2940	15.1440	1.2500	3.7560	1.367877	1.367834	+43
3	7.0685	13.4940	1.6655	3.3392	1.370662	1.370610	+52
4	8.5825	11.4595	2.0830	2.9210	1.373447	1.373379	+68
5	10.4875	10.2045	2.4753	2.5299	1.376042	1.375955	+87
6	12.2675	8.3265	2.9219	2.0827	1.378941	1.378866	+75
7	13.9270	6.6085	3.3396	1.6651	1.381630	1.381570	+60
8	15.4960	4.9165	3.7537	1.2509	1.384267	1.384223	+44
9	17.3120	3.4930	4.1710	0.8334	1.386870	1.386879	− 9

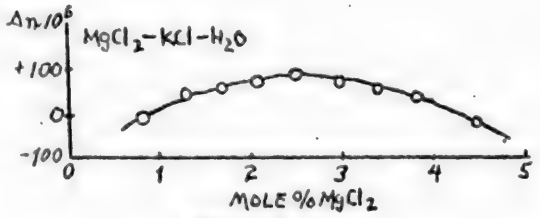

Fig. 4

System $SrBr_2$ – NH_4Br – H_2O

Table 5

Original Solutions

Name	Concentration (in mole %)	n^{20}_D
$SrBr_2$	4.5053	1.411720
NH_4Br	4.5098	1.365556

Table 6

Mixtures of $SrBr_2$ and NH_4Br Solutions

No. of mixture	Grams of original solution		Mole %		$n^{20}_{expt.}$	$n^{20}_{theoret.}$	$\Delta n \cdot 10^6$
	$SrBr_2$	NH_4Br	$SrBr_2$	NH_4Br			
1	5.6840	17.5110	0.8900	3.6090	1.374974	1.376869	1895
2	7.0505	16.1207	1.1262	3.3764	1.377440	1.379603	2163
3	9.3990	14.4055	1.4961	3.0067	1.381373	1.383783	2410
4	11.3430	12.9335	1.8047	2.6982	1.384598	1.387126	2528
5	14.1720	11.0220	2.2296	2.2738	1.388940	1.391523	2583
6	17.0040	8.6235	2.7049	1.7987	1.393898	1.396186	2288
7	18.9645	7.3000	2.9934	1.5109	1.396839	1.398889	2050
8	20.1415	6.2110	3.2072	1.2968	1.398947	1.400839	1892
9	22.2280	5.6170	3.3831	1.1209	1.400762	1.402408	1646
10	23.3090	4.4300	3.6057	0.8985	1.402999	1.404347	1348

System $BaCl_2 - KCl - H_2O$

Table 7

Original Solutions

Name	Concentration in mole %	n^{20}_D
$BaCl_2$	2.4953	1.371910
KCl	2.4903	1.357420

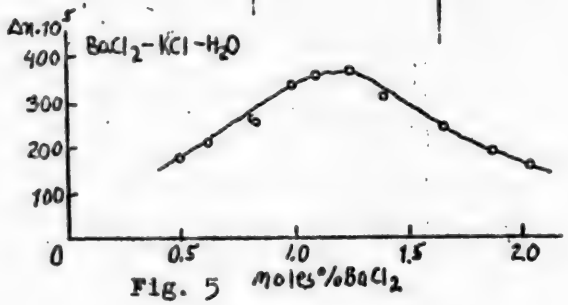

Fig. 5

Table 8

Mixtures of $BaCl_2$ and KCl Solutions

No. of mixture	Grams of original solution		Mole %		$n^{20}_{expt.}$	$n^{20}_{theoret.}$	$\Delta n \cdot 10^6$
	$BaCl_2$	KCl	$BaCl_2$	KCl			
1	4.3440	14.8240	0.499	1.993	1.360124	1.360703	179
2	5.5970	14.5010	0.618	1.874	1.361240	1.361455	215
3	7.5540	12.9190	0.831	1.662	1.362502	1.362766	264
4	9.0495	11.5860	0.998	1.495	1.363436	1.363774	338
5	10.0330	10.8140	1.103	1.390	1.364046	1.364394	348
6	11.3960	9.7400	1.247	1.246	1.364867	1.365234	367
7	12.3590	8.3315	1.394	1.099	1.365770	1.366075	305
8	15.2185	6.5365	1.660	0.834	1.367310	1.367556	246
9	17.6120	4.9730	1.875	0.620	1.368527	1.368719	192
10	17.9420	3.3630	2.046	0.448	1.369462	1.369623	161

The maximum is situated at the ratio $BaCl_2$:KCl = 1, and consequently, the compound formed may be expressed by the formula $[BaCl_3]K$.

In the system $SrBr_2 - NH_4Br - H_2O$ (Tables 5 and 6, Fig. 6) the deviation of the values of the refractive index from additivity is very great, reaching 2 units in the third decimal place. The maximum is situated at the ratio $SrBr_2$: NH_4Br = 1, permitting us to ascribe to the compound of higher order formed the

formula: $[SrBr_3]NH_4$.

The great convexity of the maximum indicates that the compound formed must be fairly stable.

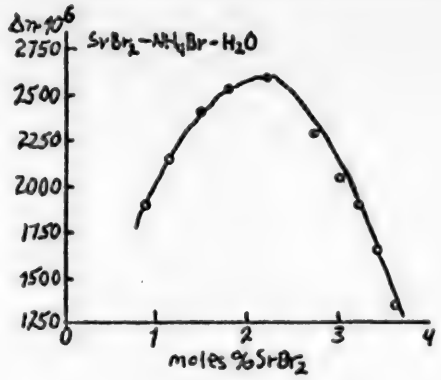

Fig. 6.

SUMMARY

1. Using the physico-chemical method of analysis of measurements of the refractive index, a study has been made of the systems:

1) $LiCl - NaCl - H_2O$,

2) $MgCl_2 - KCl - H_2O$,

3) $SrBr_2 - NH_4Br - H_2O$,

4) $BaCl_2 - KCl - H_2O$.

2. Investigation has shown the possibility of determining the formation in the systems studied of compounds of higher order by means of a significant maximum (or minimum) on the curve expressing the deviation of the values of the refractive index of the mixtures from additivity.

3. In these systems the formation of compounds of higher order has been found, with compositions: $[MgCl_3]K$, $[SrBr_3]NH_4$ and $[BaCl_3]K$.

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THE DIFFERENTIATING EFFECTS OF SOLVENTS ON THE STRENGTH OF ACIDS

V. SEPARATE POTENTIOMETRIC TITRATION OF MIXTURES OF ACIDS IN ANHYDROUS ACETIC ACID

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In our previous investigations [1-5] we showed that organic solvents, especially ketones, had a large differentiating effect on the strength of acids of different natures. We showed, for example, that in 90% acetone, the pK of hydrogen chloride equalled 2.57, of benzoic acid 9.70 (in water 4.20), of acetic acid 10.27, etc. In mixtures of mineral acids with carboxylic acids, ketones increased the exponent of the ratio between their dissociation constants by 4 to 4.5 units. We made use of this circumstance to extend the possibilities of alkalimetric and acidimetric titration.

The use of acetone and acetone mixtures permits us to carry out a separate potentiometric titration of a mixture of acids which in water are so close to the same strength that their separate titration in aqueous solution is impossible. Both for purposes of titration and for an understanding of the acid-base relationship, anhydrous acetic acid was of interest.

Acetic acid is an acid solvent whose ionic product, according to Kolthoff's [6] measurements, equals $2.5 \cdot 10^{-13}$, according to Kilpi's [17] data equals $5.3 \cdot 10^{-11}$. The dielectric constant of acetic acid is very low (equal to 6). Acetic acid has chiefly donor properties, but with respect to perchloric acid, it becomes a proton acceptor [7]. As a solvent, anhydrous acetic acid has been used in a number of investigations to study the strengths of acids and bases [8-16]. It has been found that acetic acid has a differentiating action. For example, mineral acids, of uniform strength in water, are arranged in acetic acid in the following order:

$$HClO_4 > H_2SO_4 > HCl > HNO_3,$$

which indicates the great strength of perchloric acid, while nitric acid is revealed as very weak.

In acetic acid, aminobenzoic acid is titrated like a base [17]. Amino acids are also titrated, as the bases of perchloric and sulfuric acids [18], for under the influence of the acetic acid, not only is the dissociation of the basic groups in the amino acids increased, but the dissociation of the acid groups [19] is lowered. The basic groups of gelatin have a dissociation constant in water of the order of 10^{-12}, while in acetic acid these basic groups of gelatin can be titrated like strong bases,[20].

From the data of Hall and Werner [9], Hantzsche and Langbein [13] were able to suggest that the differentiating effect of anhydrous acetic acid was sufficiently great to permit separate titration of mixtures of mineral acids that are strong in water. The purpose of the present investigation was to throw light on this possibility and to make a quantitative determination of the differentiating effect of the acetic acid.

EXPERIMENTAL

Anhydrous acetic acid was prepared from commercial glacial acetic acid, which was carefully fractionated over potassium permanganate; the 117.5-118°

fraction was then frozen three times and again fractionated over potassium permanganate under conditions which prevented the moisture of the air from entering. The absence of water was confirmed by a determination of the melting point.

The acetic acid thus prepared was used as a solvent for the preparation of solutions of perchloric, hydrochloric, sulfuric, nitric, toluenesulfonic, and trichloracetic acids. A 0.01 N solution of each of these acids was prepared by the addition of the proper weight of chemically pure acid. Water, introduced with the acids, was combined with acetic anhydride. Within the limits of accuracy of analysis, there may have been a very small excess of acetic anhydride ($\pm 0.02\%$). 10 ml of the solution of acid or a mixture of acids was taken for titration.

As a base for the titration, we used pyridine and dimethyl aniline, which behave as strong bases in acetic acid. 0.05 N solutions in anhydrous acetic acid were prepared by adding the proper amounts of the freshly distilled bases.

The titration was carried out potentiometrically, by means of an Izmailov [21] lamp potentiometer. The electrochemical cell consisted of the following chain:

$$\mathrm{Pt}\ \underbrace{\left|\begin{matrix}\text{acid}\\ \text{quinhydrone}\end{matrix}\right|\ \text{LiCl sat.}}_{\text{in } CH_3COOH}\ \Big|\ \underbrace{\begin{matrix}\text{KCl}\\ \text{sat.}\end{matrix}\ \Big|\ \begin{matrix}Hg_2Cl_2\\ \text{KCl sat.}\end{matrix}}_{\text{in } H_2O}\ \Big|\ \mathrm{Hg}$$

In the case of the acetic acid titration, a chloranil electrode was used instead of the quinhydrone, in accordance with the proposal of Conant and Hall [8], as the quinhydrone is oxidized in an acetic acid solution of nitric acid. In all the other cases, the quinhydrone electrode served excellently; its potential was quickly determined, and after a lapse of 3 to 4 minutes the potential had changed only a tenth of a millivolt.

In Fig. 1 there is a sketch of the titration vessel. Isolation from the moisture of the air was maintained by enclosing the compound under a rubber stopper and using an electrode with a mercury seal. The platinum electrode also served as a stirrer. The surface of the electrode covered 3 cm^2. The left part of the siphon was filled with a saturated solution of LiCl in acetic acid, contact being made across a thin section. The right half of the siphon was filled with a saturated aqueous solution of KCl in agar-agar in order to diminish the resistance.

The titration was carried out at room temperature, which over a long period varied from 18 to 20°.

In studying the electrolytes in acetic acid, as the solvent had a low dielectric constant, it was necessary to consider the influence of the salt effect. In order to eliminate this, we introduced into the solution of acid being titrated a 0.01 N solution of lithium chloride.

In this way, solutions of $HClO_4$, HCl, H_2SO_4, HNO_3, CCl_3COOH and $CH_3C_6H_4 \cdot SO_3H$ were titrated. During the titrations we observed an interesting phenomenon, of which we shall speak below, in considering the results. Here we shall only indicate the fact that trichloracetic acid could not be titrated in anhydrous acetic acid. In the titration of perchloric acid, we sometimes found two points of inflection on the titration curve (Fig. 2).

The titration of mixtures of these acids is of great interest. The results given below are a solution to an extremely difficult analytical problem, and clearly confirm the fact that an evaluation of the strength of an electrolyte according to its behavior in water is misleading. The strength of an electrolyte is determined by the solvent.

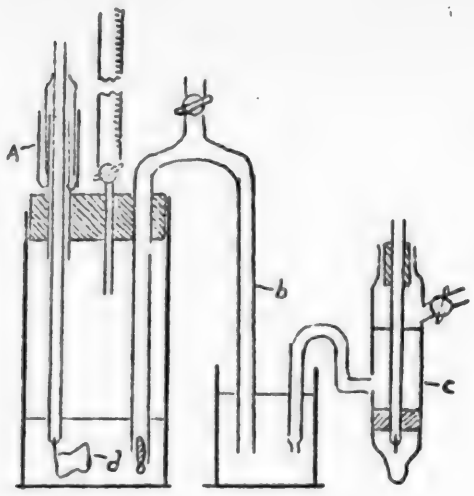

Fig. 1. Titration Vessel.

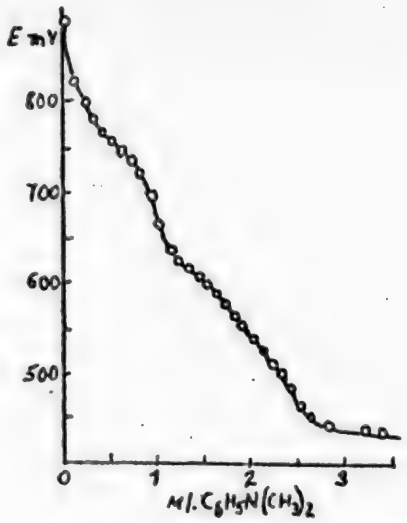

Fig. 2. Curve of titration of perchloric acid with dimethyl aniline. Chloranil electrode.

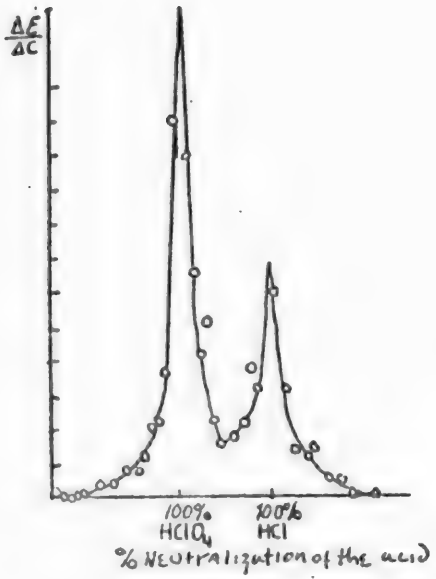

Fig. 3. Titration of mixtures of perchloric and hydrochloric acids with pyridine.

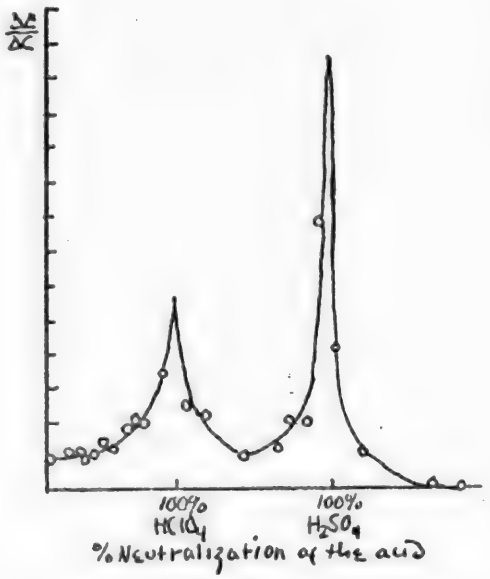

Fig. 4. Titration of mixtures of perchloric and sulfuric acids with pyridine.

For the titration of acid mixtures, 5 ml of a solution of each acid was taken, and the mixture was titrated in the manner described above. Mixtures of $HClO_4$ and H_2SO_4, $HClO_4$ and HCl, HCl and CCl_3COOH, and HNO_3 and $CH_3C_6H_4 \cdot SO_3H$ were titrated. The last pair was titrated with a chloranil electrode, all the others with a quinhydrone electrode. Results of the titration of mixtures are given in Figs. 3, 4, and 5. They completely confirm our belief that anhydrous acetic acid differentiates sufficiently between the strengths of acids to permit the separate titration of acids which in water, alcohol, and even in a differentiating solvent like acetone can not be titrated separately.

As was indicated above, trichloracetic acid could not be titrated in acetic acid. Neither could it be titrated in mixtures with mineral acids, but in this case, the separate amounts of both trichloracetic and mineral acid could be determined by a double titration: titration of the mixture in aqueous solution gives the total acidity, titration in acetic acid the amount of mineral acid.

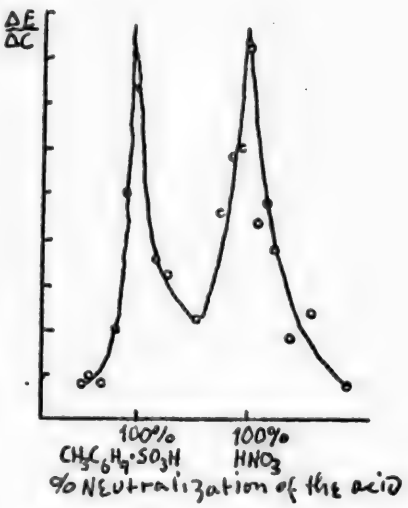

Fig. 5. Titration of mixtures of toluenesulfonic and nitric acids with dimethyl aniline.

Evaluation of Results

In the titration of sulfuric acid with pyridine, in the case where there was a possible excess of acetic anhydride, sulfuric acid behaved like a mono-monovalent electrolyte. The jump in potential on approaching the equivalent point was fairly great. This speaks for the great strength of this acid in anhydrous acetic acid.

This interesting phenomenon has been observed by other investigators. Russell and Cameron [18] showed that with aniline guanidine, and diethyl-o-toluidine, sulfuric acid is titrated as dibasic, while with sodium acetate it is incompletely titrated. The authors assume that in the presence of an excess of acetic anhydride, there is the formation of a product from it and the sulfuric acid — a mixed anhydride of sulfuric and acetic acids. This compound has ultra acid properties. Hutchison and Chandlee [22] consider sulfuric acid in acetic acid solution as a mono-monovalent electrolyte. Hall and Voge [23], from the results of measurements on the electrical conductivity of sulfuric acid, find that in acetic acid it behaves like a weak monobasic acid with pK = 8.2.

Similar anomalies have been observed with other acids than sulfuric. Russell and Cameron have suggested that in the case of an excess of acetic anhydride, there are two forms of perchloric acid present; their reason is that the titration curve of perchloric acid in their experiments has two points of inflection. It has been indicated above that in certain cases, this phenomenon was also observed in our experiments. In addition, in one case we observed two points of inflection for the hydrochloric acid titration curve as well.

According to Usanovich [24], acetic anhydride is an amphoteric compound; therefore it is very probable that it does have an influence. But the question cannot be decided on the basis of existing experimental data, as various invest-

igators have prepared solutions in different ways, and in almost all instances have not excluded the possibility of an excess ($\pm$) of acetic anhydride. To decide this question, we intend to undertake a special investigation; in addition, the nature of electrolytes in acetic acid will be determined under the influence of the solvent itself, of the anhydride, and possibly of the character of the base used for titration, and finally, we shall take account in all this of the salt effect.

It is of interest to estimate the strength of the differentiating effect of anhydrous acetic acid. The fact that it was possible, in acetic acid, to carry out separate titrations of mixtures of acids, testifies to the fact that $HClO_4$ behaves like a strong acid, H_2SO_4, HCl, and HNO_3 like weak acids. After perchloric acid comes toluenesulfonic acid, as this acid can be titrated separately in mixtures with nitric acid, but sulfuric and hydrochloric acids cannot be. On the other hand, nitric acid cannot be titrated in the presence of sulfuric and hydrochloric acids. On this basis, we can draw up the following series:

$$HClO_4 \gg CH_3C_6H_4 \cdot SO_3H > H_2SO_4 > HCl > HNO_3,$$

agreeing with the series of Hantzsche and Langbein, which was obtained from data on electrical conductivity.

From the titration curves of the acid mixtures, we have made a quantitative estimate of the differentiating effect of acetic acid with regard to the quantity $\left(\frac{\Delta E}{\Delta C}\right)_1$%, i.e., with regard to the jump in potential on approaching the equivalent point, which is characterized by the ratio of dissociation constants of the acids [2]. It has been shown that the ratio of the dissociation constants of perchloric and sulfuric acids amounts to 4.5 units in the exponent, and of perchloric and hydrochloric to 6.2, i.e., perchloric acid is more than 10,000 times stronger than sulfuric acid and more than 1,000,000 times stronger than hydrochloric acid. Consequently, the ratios of dissociation constants completely confirm the conditions for accurate separate titration [25].

One of us [27], on the basis of the data of Hantzsche and Langbein, Kolthoff, and Willman on the electrical conductivity of acetic acid solutions of mineral acids, has calculated their dissociation constants. The values obtained are given in a table (Column 2). They confirm the series of acids given above. But the ratios of dissociation constants calculated from electrical conductivity data are less than the ratios of the constants from potentiometric titrations. The fact that in acetic acid it is possible to titrate mixtures of mineral acids separately testifies to a greater differentiating effect of acetic acid than does the ratio of the constants calculated from electrical conductivity data.

It is not without interest to consider several peculiarities of the differentiating effect of acetic acid as an acid solvent, and to compare it with the influence of liquid ammonia on acids and bases, for the latter is a solvent with clearly expressed basic properties [28]. The first peculiarity of acetic acid consists in the fact that the number of compounds exhibiting acid properties in it is much less than in water. Even nitric acid shows only weakly acid properties in anhydrous acetic acid solution: it can be titrated separately in mixtures with

Dissociation constants of acids in acetic acid in in liquid ammonia [27]

Acid	pK_{CH_3COOH}	pK_{NH_3}
$HClO_4$....	5.80	2.27
HBr.....	6.40	0.62
H_2SO_4....	8.20	–
HCl.....	8.85	0.87
HNO_3.....	9.38	0.37
CCl_3COOH.	11.46	–

toluene-sulfonic acid, and shows a trifling catalytic effect [13]; trichloracetic acid too, which is very strong in water, is so weak in acetic acid that it cannot be titrated as an acid. The dissociation of the acid groups in amino acids decreases to such an extent that amino acids in acetic acid can be titrated as bases, i.e., they do not exhibit acid properties. By analogy, the number of bases in liquid ammonia cannot be great [25].

The second peculiarity consists in the fact that acetic acid sharply differentiates the strength of acids, weakening them considerably, while liquid ammonia has a leveling effect, increasing the strength of weak acids. Prussic acid, which is very weak in water, develops the properties of a strong acid in liquid ammonia.

The opposite phenomenon can be observed with regard to bases. The number of bases grows in acetic acid, and their strength increases. The number of bases in ammonia, as already indicated, is small.

Both acetic acid and liquid ammonia have low dielectric constants. Therefore the reciprocal electrostatic effects of ions in both solvents are greater than in water. But the protolytic properties of these solvents are of an opposite nature. Acetic acid is a proton donor, while liquid ammonia is a solvent with definite acceptor properties. Therefore, the difference in the influence of these two solvents on the strength of acids is related to the difference in protolytic properties.

SUMMARY

1. Anhydrous acetic acid has a differentiating effect on acids which are strong in water. This property of acetic acid is great enough to permit the separate titration of mixtures of the following acids: $HClO_4 + H_2SO_4$, $HClO_4 + HCl$, $CH_3C_6H_4 \cdot SO_3H + HNO_3$.

2. The strength of acids is decreased in anhydrous acetic acid. The titration curves show that perchloric acid is the strongest; it is more than 10,000 times stronger than sulfuric acid and more than 1,000,000 times stronger than hydrochloric. Dissociation constants of the mineral acids in acetic acid have been calculated from electrical conductivity data.

3. It is shown that a number of anomalies in the titration of anhydrous acetic acid are related to the possibility of the presence of acetic anhydride, and to the nature of the base used for titration. These anomalies are being investigated.

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THE CHEMICAL STABILITY OF FELDSPARS IN ACID SOLUTIONS

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The behavior of feldspars in solutions of acid is of great interest from various points of view. It is the feldspars in particular, under the action of humic acid, which to soil scientists broadly represent the decomposition of aluminosilicates. The decomposition of mineral rocks under the influenceof biological processes which take place upon their surfaces is regarded by many investigators a as due to the elimination of organic acids by plants. The film formed on the mineral neogenically regulates the further course of decomposition and acts to provide a source of nutrients for the plant. On the other hand, the study of the chemical stability of feldspars in mineral acids is of interest because of its possible application in the ceramic industry (analysis of raw materials, stability of of products). And finally, the behavior of aluminosilicates in solutions of acids characterizes their structure, the stability of their skeleton.

The methods of investigation of the chemical stability of feldspars used by various authors are very similar. They usually include crushing the sample to a powder of a definite mesh, treatment with the appropriate reagents, and an analysis of the filtrate.

In all this, the various investigators have varied the temperature of treatment, the time, and the pressure. The powder methods have the fault that the calculated values of the surface which undergoes decomposition can be determined only very approximately. This circumstance makes it difficult to compare the results of different investigators. In addition, the powder method gives no idea of the neogenic influence on the course of decomposition of the mineral.

The question as to whether the films formed on crystalline aluminosilicates are factors regulating the velocity of their decomposition in the reaction with solutions has hardly been touched in the literature.

As is well known, I.V.Grebenshchikov and his coworkers long ago found that films of silica were formed on silicate glasses as a result of treatment with solutions of acid, and he developed methods of determining the thickness of these films [1]. Later, Correns suggested that aluminosilicate films were formed in the reaction of adularia and leucite with solutions of different pH [2]. However, he calculated the thicknesses of these films indirectly by determining the amount of oxides that had gone into solution. He was unable to determine the change in t the aluminosilicates treated either by roentgenographic or optical methods.

The aim of the present investigation was to study the initial stages in decomposition of natural albite, plagioclase-oligoclase, and microcline under the action of acid solutions.

In this work, we utilized essentially the method developed in the laboratory of I.V.Grebenshchikov for determining the thickness of surface films on glasses, by means of a measurement of the elliptic polarization of reflected light [3].

Reflection from the surface of a glass that is not freshly polished changes

plane polarized into elliptically polarized light. According to Drude's theory, this phenomenon is due to the presence upon the surface of a layer with a different refractive index.

As the investigations of N.F.Timofeyeva [3] have shown, Drude and Grossmuller's formula for the calculation of the optical thickness of the films applies for thin films up to 0.1 wave length.

As the feldspars we investigated were very stable and their decomposition under the conditions we used took place very slowly, the calculation of the optical thickness of the surface films could be satisfactorily carried out by Drude's formula:

$$\frac{d}{\lambda} = \frac{\rho}{\pi \sqrt{n^2 + 1}} \frac{n + 1}{n - 1} ,$$

where d is the optical thickness of the film; λ is the wave length of the light from the source used, equal for the green line of mercury to 5461 Å; ρ is the coefficient of ellipticity equal to $\tan \varphi$; φ is the angle of ellipticity; n is the index of refraction.

The optical thicknesses of the films determined from this formula are proportional to the depth of decomposition. The measurement was carried out with a polarization spectrometer, described in detail in the above-cited work of N.F. Trimofeyeva.

The chemical composition of the feldspars investigated is given in Table 1.

TABLE 1 *

Name of feldspar	Composition (in weight %)						
	Na_2O	K_2O	CaO	MgO	Al_2O_3	SiO_2	total
Albite.....	10.75	–	0.25	0.11	20.52	68.07	99.87
Crystalline oligoclase	10.25		3.10	–	22.72	64.08	100.15
Vitreous oligoclase....	10.61		2.64	–	22.20	64.68	100.13
Crystalline microcline	4.35	10.85	0.19	0.20	19.27	64.88	99.74
Vitreous microcline....	4.26	11.76	0.30	0.09	19.20	64.04	99.65

From these analyses we calculated the mineralogical composition of the minerals in the following manner. All the CaO was calculated as anorthite, the K_2O as potash feldspar.

After subtracting the amount of anorthite and potash feldspar, the SiO_2 in the residue was calculated as albite. In the mineral of the same name, albite was calculated from the Na_2O content.

The resulting composition of the minerals investigated is given in Table 2.

TABLE 2

Name of mineral	Anorthite	Potash feldspar, weight %	Albite	$mSiO_2 - nAl_2O_3$
Albite	1.04		90.86	7.69
Microcline	0.95	64.10	33.47	–
Orthoclase	15.38	–	83.58	–

* Analyses carried out by K. S. Chernisheva.

Thus, microline contains an admixture of almost pure albite.

Because of its anorthite content, the oligoclase was considered to be plagioclase No. 15. The index of refraction of such a plagioclase should be equal to 1.544. An experimental measurement gave the value 1.543.

Our measurements gave the specific gravities of both oligoclase and microcline as being equal to 2.60..

The specimens of oligoclase and microcline were cut parallel to the planes of the first pinacoid to give a parallelepiped with dimensions 20 x 20 x 10 mm. The specimens were polished, after which the absence of films was checked by measuring their elliptic polarization. The usual optical thickness of the films in the minerals investigated before treatment did not exceed 20 Å. As the albite at our disposal was in the form of a finely crystalline aggregate, it did not appear possible to section it parallel to any determined face to give a specimen. It was cut arbitrarily. The samples of the above-described minerals were maintained in the proper solutions in a thermostat at 40° for different lengths of time. Then they were washed with warm distilled water and dried one hour at 105°.

After this treatment, the thickness of the film was measured on different planes of the specimen by the method described above.

With the purpose of investigating the influence of structure upon the chemical stability of feldspars, the vitreous forms were studied along with the crystalline specimens. These were obtained by melting the microcline and oligoclase described above in a Silit oven. About 100 g of mineral (an unbroken lump) was placed in a fireclay crucible in the cold oven, which was heated up to 1350°. The mass was kept at this temperature for 2 hours, after which the oven was disconnected and the crucible slowly allowed to cool. The crucible was then smashed, and the mass was removed for inspection of the feldspar glass from the center, which was not in contact with the walls of the crucible. A chemical analysis was carried out on the feldspar glass thus obtained. The data of analysis are given in Table 1. The index of refraction for the vitreous microcline was 1.491, for oligoclase 1.512. The respective specific gravities were 2.41 and 2.43. A comparison of the chemical stability of the crystalline and vitreous feldspars was made by two methods: by the measurement of elliptic polarization and by a conductometric method, described in detail in the work of A.G.Samartsev and V.S.Molchanov [4]. In the latter test, the above minerals were ground to a powder, and the fraction of mesh 50 to 70 microns was removed. The screened powder was washed free of turbidity with alcohol, and dried over calcined copper sulfate.

A weighed sample of the mineral, corresponding to 1 cm^3 of powder, was subjected to the action of 0.001 N HCl solution at 25°. The specific electrical conductivity of the solution was determined after a lapse of time. The depth of decomposition $\underline{h}$ was calculated from the formula:

$$h = \frac{(x_0 - x_t)}{290} \frac{v}{\varepsilon \alpha \rho},$$

where x_0 and x_t are the specific electrical conductivity of the solution at the beginning of the experiment and at a given moment; $\alpha = \frac{\% \text{ oxide}}{100 \cdot \text{equiv. weight}}$ specific gravity; $\underline{v}$ is the volume of liquid; ρ the total surface of the powder.

In order to determine which particular oxides went into solution in this case, we carried out a qualitative microchemical analysis of the liquid after the experiment, testing for sodium ion, Al_2O_3, and SiO_2. We observed only the sodium ion in solution. The passage of CaO into the solution obviously took place (the

solubility of anorthite in acids is generally known). The stability of the albite and the anorthite, as we shall see below, is of the same order. Therefore, in calculating the value of $\varepsilon\alpha$, we took into account only α Na_2O, K_2O, and CaO.

As in this method the determination of the size of surface of the powder is not very accurate, we carried out parallel experiments for each specimen.

In applying the method of elliptic polarization, the chemical stability of the specimens was tested in 0.5 N solutions of hydrochloric and sulfuric acids; in 0.5% acetic acid at 40°.

The results are given in Table 3 and in Figs. 1 and 2. Columns 5 and 6 of this table contain the values of the angle of ellipticity before and after treatment, 7 and 8 list the calculated optical thickness of the surface layer.

The data on the chemical stability of the crystalline and vitreous feldspars, measured conductometrically, are given in Table 5 and in Fig. 3.

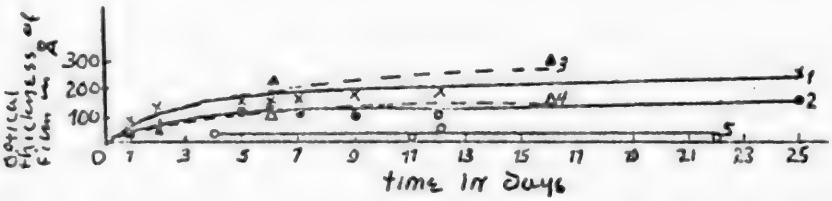

Fig. 1. Chemical stability of oligoclase and albite in 0.5 N solutions of HCl and H_2SO_4 at 40°.

1-oligoclase, face [100] in HCL; 2-oligoclase, faces [010] and [001] in HCL.
3-oligoclase, face [100] in H_2SO_4; 4-oligoclase, faces [010] and [001] in H_2SO_4;
5-albite in HCL.

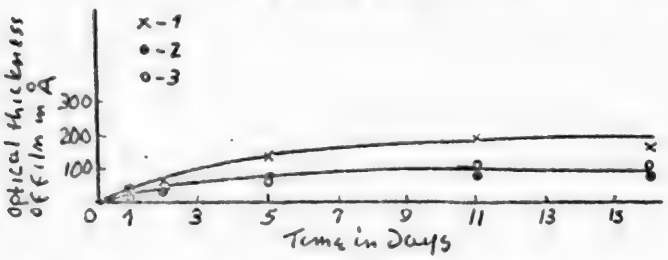

Fig. 2. Chemical stability of crystalline and vitreous oligoclase in 0.5N solution of HCl at 40°.

1-oligoclase, face [100]; 2-oligoclase, faces [010] and [001];
3-vitreous oligoclase.

As can be seen from Table 3 and Fig. 1, oligoclase shows a tendency to decompose in solutions of hydrochloric and sulfuric acids.

As a result of decomposition on the surface of the mineral, an aluminosilicate film is formed with a lower index of refraction than that of the mineral itself. The velocity of growth of the thickness of the film slows down in the course of time, as a result of the protective action of the surface layer, which makes it more difficult for the reagent to penetrate to the inner layers of the mineral.

The different faces of oligoclase are characterized by differences in

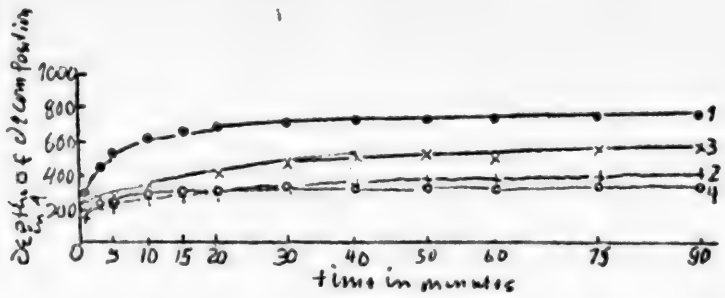

Fig. 3. Determination of the chemical stability of feldspars by a conductometric method.

1-crystalline oligoclase; 2-vitreous oligoclase; 3-crystalline microcline; 4-vitreous microcline.

chemical stability: the velocity of decomposition is maximal parallel to the first pinacoid [100]. Parallel to the planes of cleavage (pinacoid [010] and [001]) decomposition takes place more slowly. For example, after 25 days in the 0.5 N solution of HCl at 40°, the optical thickness of the film formed on pinacoid [100] is 280 A, while on pinacoid [010] it is 149 A.

The curves which characterize the action of the acid solution on the different faces of oligoclase have a similar character. Only, in the case of face [100], the decomposition curve is relatively high.

Decomposition in sulfuric acid takes place more quickly than in hydrochloric at the same concentration; at the same time, the comparative chemical stabilities of the different faces remain unchanged.

The phenomenon described above is in our opinion the result of the following circumstance.

Feldspar, as is known, belongs to the type of so-called "bound" structures, which are characterized by the presence of a three-dimensional framework of alumino-silicate and silicic acid tetrahedra bound to each other in the form of quadruple and octuple rings.

This alumino-silicate framework is a sort of giant anion. Cations (alkaline and alkaline earth) with a charge equivalent to that of the anion, are situated in large hollow spaces in the octuple ring [5].

In the process of treatment with acid, under our conditions, the skeleton remains essentially unchanged, as is shown by microchemical analysis of extracts. The cations are leached out. The penetration of the reagent to the cations varies for the different faces. The first pinacoid, characterized by the presence of narrow, hollow spaces, which form quadruple rings, offers the most favorable condition for this. Apparently, it also is possible to explain in this manner the great velocity of decomposition along face [100].

Upon melting, the feldspar forms a disordered, continuous, network, in which the hollows of the quaternary rings (if quaternary rings still exist) may overlap, and the leaching out of the cations must take place more slowly.

And in fact, upon comparison of the chemical stability of the crystalline and molten oligoclase on treatment with 0.5 N HCl solution, it is found that the decomposition of the vireous form takes place more slowly than that of the crystalline parallel to the first pinacoid (Table 3, Fig. 2).

In the case where the chemical stability was measured conductometrically, we excluded the possibility of investigating the velocity of decomposition along the individual faces.

TABLE 3

Results of experiments on the chemical stability of albite and orthoclase in acids by the method of elliptic polarization

Name of specimen	Name of acid	Temp.	Duration of treatment, days	φ		Optical thickness (A)	
				before treatment	after treatment	before treatment	after treatment
.....	HCl 0.5 N solution	40°	4	–	28'	–	37
			7	12'	10'	16	13
Albite.....			11	–	18'	–	24
			12	16'	41'	22	54
			22	11'	11'	14	14
	CH_3COOH 0.5%	40°	5	–	14'	–	19
			9	–	20'	–	26
			16	–	28'	–	37
oligoclase first series:							
pinacoid [100]	HCl 0.5 N solution	40°	1	13'	1° 1'	17	79
			2	9'	1° 40'	12	129
			5	13'	2°	17	155
			6	20'	1° 58'	26	151
			7	10'	2° 3	13	159
			9	–	2° 9'	–	168
			12	–	2° 14'	–	173
			25	–	3° 17'	–	253
pinacoid [010] and [001]			1	–	27'	–	35
			2	–	29'	–	37
			5	0	1° 26'	0	111
			6	20'	1° 32'	26	118
			7	–	1° 21'	–	102
			9	–	1° 16'	–	98
			12	–	1° 20'	–	102
			25	–	2° 6'	–	162
2nd series:							
pinacoid [100]	HCl 0.5 N solution	40°	1	8'	34'	10	43
			2	5'	49'	6	62
			5	15'	1° 48'	19	139
			11	30'	2° 28'	38	191
			16	23'	2° 5'	29	162
pinacoid [010] and [001]	HCl 0.5 N solution	40°	1	10'	26'	13	33
			2	7'	27'	9	35
			5	17'	1'	22	77
			11	28'	1° 1'	36	78
			16	30'	1° 3'	38	80
vitreous	HCl 0.5 N solution	40°	1	6'	34'	8	46
			2	0	26'	0	35
			5	7'	43'	9	61
			11	0	1° 24'	0	112
			16	–	1° 19'	–	106
oligoclase pinacoid [100]	H_2SO_4 0.5 N solution	40°	2	–	56'	–	72
			6	–	2° 53'	–	222
			16	–	3° 36'	–	280
pinacoid [010] and [001]	H_2SO_4 0.5 N solution	40°	2	–	32'	–	40
			6	–	1° 21'	–	105
			16	–	1° 57'	–	147

TABLE 3 (Contd.)

Name of specimen	Name of acid	Temperature	Duration of treatment, days	Optical thickness (A) before treatment	Optical thickness (A) after treatment	Optical thickness (A) before treatment	Optical thickness (A) after treatment
pinacoid [100]	CH_3COOH 0.5%	40°	1	–	23'	–	30
			5	–	20'	–	26
			9	–	23'	–	30
			16	–	26'	–	34
pinacoid [100]	$C_2H_2O_4$ N solution	40°	6	15'	30'	19	38
			13	20'	55'	26	71

However, even in this case, the decomposition curve of the vitreous specimen is lower than the curve of the crystalline one (Table 5, Fig. 3).

Both curves are similar, and show the slowing down of the decomposition with time.

It is of interest to note that in an investigation of the chemical stability of albite toward 0.5 N HCl solution by the method of elliptic polarization, no decomposition was observed (Table 3, Fig. 1). Even a long stay in the acid solution, for 22 days, did not change the optical thickness of the film in comparison with the original. During the same period, the surface of the oligoclase described above formed a film whose optical thickness was greater than 200 A. From this it would seem possible to draw the conclusion that only the anorthite molecules in oligoclase are decomposed, as several investigators have suggested. However, this supposition is not confirmed. Analysis of the hydrochloric acid extract of the oligoclase we investigated showed a large amount of sodium, while that from albite showed negligible traces. These facts, apparently, are explained by the circumstance that oligoclase forms a series of solid solutions of anorthite-albite, which have a single crystalline structure. The decomposition of the oligoclase will be distinct both from the extremely stable albite, as well as from the easily decomposed anorthite.

Table 4 gives the velocity of decomposition of microcline in 0.5 N solution of hydrochloric acid, as determined by the method of elliptic polarization. As can be seen from the data given, microcline, like albite, is extremely stable. Even after being kept in the solution of hydrochloric acid for a period of 140 days, there was no noticeable formation of a film.

We must observe that the specimens of microcline changed in external appearance upon long treatment. During this change, a fine threadlike layer was observed, in the form of decomposed material. Apparently, decomposition took place because of a layer of plagioclase, which, according to the figures of our analysis, was present in our specimens in small amounts. In this regard, the method of elliptic polarization was extremely valuable, for it characterized the chemical stability of the main material, and was not affected by the small amounts of impurity, if the latter were present in the form of separate inclusions.

A comparison of the chemical stability of vitreous and crystalline microcline by means of the conductometric method showed the latter to be less stable. The decompsoition curve of the crystalline microcline lies above the other (Fig. 3). As microcline, both in the vitreous and in the crystalline form, produces no film on the surface upon treatment with 0.5 N HCl, it is possible that the change in the specific electrical conductivity of the solution by the conductometric method is essentially dependent upon the decomposition of the plagioclase.

TABLE 4

Results of experiments on the chemical stability of microcline in acids by the method of elliptic polarization

Face tested	Acid	Temp.	Duration of treatment, days	φ before treatment	φ after treatment	optical thickness (A) before treatment	optical thickness (A) after treatment
1	2	3	4	5	6	7	8
pinacoid [100]	HCl 0.5 N solution	40°	1	5'	23'	7	30
			2	17'	36'	23	48
			3	19'	22'	25	29
			5	25'	25'	34	34
			12	28'	32'	36	40
			27	20'	26'	26	32
			54	20'	25'	26	32
			90	14'	0	18	0
			140	26'	52'	33	67
pinacoid [010]	HCl 0.5 N solution	40°	1	20'	32'	26	41
			2	19'	33'	24	42
			3	34'	36'	44	48
			5	40'	43'	53	58
			12	—	49'	-	63
			27	55'	32'	71	41
			90	35'	12'	47	16
Vitreous	HCl 0.5 N solution	40°	2	- 7'	2'	—	3
			5	- 2'	30'	—	43
			12	- 5'	55'	—	79
			25	+ 2'	48'	3	70
			40	0	48'	0	70
pinacoid [100]	H_2SO_4 0.5 N solution	40°	2	5'	16'	7	21
[010]			2	6'	32'	8	41
[100]			6	8'	19'	10	25
[010]			6	18'	20'	24	26
[100]			16	—	14'	—	19
[100]			90	—	34'	—	44
vitreous	H_2SO_4 0.5 N solution	40°	16	—	49'	—	63
pinacoid [100]	CH_3COOH 0.5%	40°	1	—	38'	—	47
[100]			5	—	26'	—	34
[010]			5	—	47'	—	65
[100]			16	—	11'	—	14
[010]			16	—	16'	—	21
[100]			23	—	16'	—	21
	$C_2H_2O_4$ 1 N solution	40°	6	0	30'	—	38
			13	-1'	1'	—	1

As is obvious from the data of Tables 3 and 4 the action of such organic acids as acetic and oxalic on feldspar is weaker than the action of mineral acids.

Thus, from the results given, it follows that the method of elliptic polarization is extremely valuable for investigating the chemical stability of feldspars to acids. By means of it we can observe and measure the surface film which regulates the velocity of decomposition of the mineral. In addition we can determine

TABLE 5

Results of experiments on the chemical stability of feldspars in 0.001 N HCl solution by the conductometric method

Name of specimen	Depth of decomposition (in A) after time (in minutes)											
	1	3	5	10	15	20	30	40	50	60	75	90
crystalline oligoclase	320	470	555	657	676	716	740	777	790	790	802	820
	284	458	512	598	655	667	704	698	685	692	704	722
vitreous oligoclase	173	225	242	251	276	298	358	342	382	406	429	437
	120	186	202	242	266	278	312	342	380	342	365	365
microline crystalline	252	266	280	352	–	410	491	510	530	500	563	563
microline vitreous	–	234	234	284	299	299	334	334	334	310	334	334
microline crystalline at 40°	324	324	324	350	397	410	456	511	555	555	530	555

the velocity of decomposition in relation to the crystallographic direction.

The above indicated factors do not hold with regard to the use of the various powder methods.

In an investigation of the influence upon feldspar of reagents which act upon the aluminosilicate skeleton, we may expect to find other laws which influence the course of the decomposition.

We are conducting an investigation in this direction.

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POLAROGRAPHIC INVESTIGATION OF STYRENE IN AN ALCOHOLIC SOLUTION OF TETRABUTYLAMMONIUM IODIDE

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INTRODUCTION

The polarographic investigation of styrene is of great theoretical and practical interest.

It is of theoretical interest because the polarographic method offers the possibility of clearing up several questions concerning the mechanism of the reduction of styrene at the mercury dropping electrode.

Its practical interest lies in determining what possibility there is of devising a polarographic method for the rapid and accurate determination of styrene in the products of treated coal.

We have found only a single reference [1] in the literature which indicates the possible reduction of styrene on the mercury dropping electrode. The potential of a half-wave of styrene equals 2.35 volts (with reference to a sat. calomel electrode) in a 0.175 M solution of tetrabutylammonium iodide in 75% dioxane.

EXPERIMENTAL

In this research we set out to find a more suitable and less difficultly available solvent for styrene and to conduct a detailed polarographic investigation of the styrene wave in order to obtain a complete polarographic characterization of this wave, as well as to shed light on the possibility of utilizing this wave for the quantitative determination of styrene.

The polarographic study of styrene was carried out in parallel in two sets of apparatus: with a visual polarograph, constructed by UFAN (Sverdlovsk) and with a photopolarograph constructed by Giredmet (Odessa).

In all the experiments, an electrolyzer with an internal anode was used; this was in the form of a small vessel 8 to 9 cm high, diameter 10 to 12 mm. The volume of electrolyte was equal to 1.0 ml. As a comparison electrode (anode) mercury was used at the bottom, connected with the positive pole by means of a platinum wire sealed to the electrolyzer. The anode potential was determined relative to a saturated calomel electrode by means of a potentiometer. To measure the diffusion current during the investigation of styrene, the salt tetrabutylammonium iodide was used as an electrolyte in the form of a 0.2 M solution in 75% ethyl alcohol. As our experiments showed, the use of ethyl alcohol instead of dioxane (which had been used in the work of Laitinen and Wawzonek [1]) permitted us to obtain a complete record of the styrene wave. From the practical point of view, also, ethyl alcohol has the great advantage over dioxane that it is much more available. As a solvent for styrene we used a water-alcohol mixture containing 75% (by volume) of the ethyl alcohol. In this solvent 200 to 300 millimoles/liter of styrene dissolved readily.

The concentration of styrene in the experiments was from 1 to 30 mmoles/l. No oxygen was given off from the solution, as both waves of oxygen have a much greater positive half-wave potential (−0.1 and −0.9 volts with reference to the sat. cal. elec.) and therefore in the range of the potentials used in our work (from − 2.0 to − 2.9 volts with ref. to sat. cal. elec.), the diffusion current of oxygen will have a certain small constant value and will not affect the accuracy of the measurement. No special substances with surface-activity were added to the solution, as tetrabutylammonium iodide itself has surface-activity.

Fig. 1 gives the residual current of the solution of 0.2 M $(C_4H_9)_4NI$ in 75% alcohol. Inasmuch as the height of the styrene wave was measured at potentials of − 1.7 and − 2.1 volts (with respect to the mercury on the bottom) the figures obtained show that tetrabutylammonium iodide is a very good electrolyte for the polarographic study of styrene, as in this interval of the change in potential the residual current is small and amounts to 0.4 to 0.45 μA, and the final increase on the polarogram is equal to − 2.9 volts (with ref. to sat. cal. elec.). Styrene was obtained in the laboratory by the decarboxylation of cinnamic acid [2] and had the following constants: specific gravity d^{20} 0.9070 and refraction n_D^{20} 0.5395.

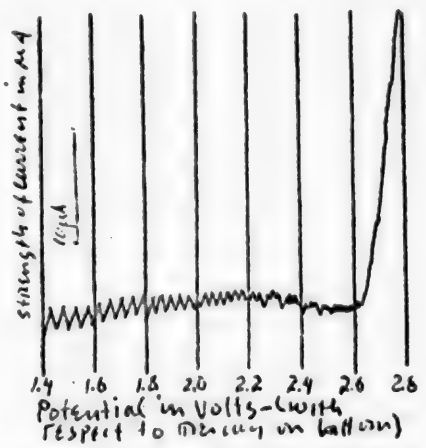


Fig. 1. Polarogram of 0.2 M tetrabutylammonium iodide in 75% ethyl alcohol (residual current).

Tetrabutylammonium iodide was synthesized by a method described in the literature [1], with minor changes, by one of the authors of this article, and melted at 142° (literature data give the melting point as 141 to 142°).

In order to obtain a polarogram, an initial solution of styrene was prepared in 75% ethyl alcohol, usually 250 to 270 mmoles/l, (this corresponds approximately to two drops of styrene in 1 ml of solution).

1 ml of a solution of 0.2 M tetrabutylammonium iodide in 75% alcohol was placed in a dry electrolyzer and a few drops of the initial solution of styrene then added to it (final concentration from 1 to 30 mm/l of styrene).

Upon measuring the solution with the polarograph, an excellent picture of the styrene wave was obtained (Fig. 2).

Polarographic Investigation of the Styrene Wave

The potential of the half wave was calculated from the equation of the wave given by the relation between halfwave potential and current strength at any point of the polarographic curve. A graph of the equation of the wave in coordinates $\log \frac{i}{I - i}$ as a function of E (i is the current strength at potential E; I is the diffusion current) is expressed as a straight line with angular coefficient

$$\frac{0.0596}{n}.$$

The experimental data obtained for the styrene wave and the relationship $\frac{i}{I - i}$ as a function of E, are given in Table 1 and in Fig. 3.

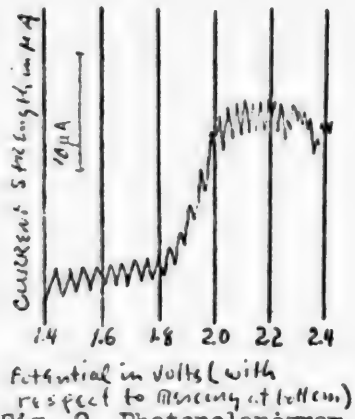


Fig. 2. Photopolarogram of a styrene solution in a solution of 0.2 M tetrabutylammonium iodide in 75% ethyl alcohol.

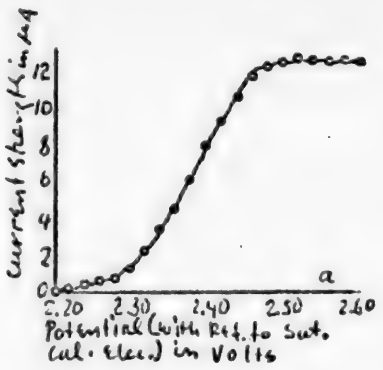


Fig. 3. Polarogram of a solution of 10.4 mmole/l of styrene in 0.2 M tetrabutyl ammonium iodide in 75% ethyl alcohol, obtained with visual polarograph (current strength corrected for residual current).

TABLE 1

Cathode potential (in volts with ref. to sat. cal. elec.)	Current strength μ A	$\log \frac{i}{I-i}$	Cathode potential (in volts with ref. to sat. cal. elec.)	Current strength μ A	$\log \frac{i}{I-i}$
− 2.18	0	−	− 2.34	3.30	$\bar{1}.55$
− 2.20	0.15	$\bar{2}.08$	− 2.36	4.50	$\bar{1}.74$
− 2.22	0.30	$\bar{2}.38$	− 2.38	6.0	$\bar{1}.96$
− 2.24	0.45	$\bar{2}.57$	− 2.42	9.1	0.42
− 2.26	0.60	$\bar{2}.70$	− 2.44	10.5	0.70
− 2.28	0.75	$\bar{2}.80$	− 2.46	11.7	1.11
− 2.30	1.35	$\bar{1}.08$	− 2.48	12.3	1.61
− 2.32	2.25	$\bar{1}.34$			

TABLE 2

No. of experiment	Concentration of styrene (mmole/l)	Concentration of $(C_4H_9)_4NI$ in 75% alcohol	Half-wave potential (volts) with ref. to mercury on bottom	Half-wave potential (volts) with ref. to sat. cal. elect.
1	2.50	0.1 M	− 1.98	− 2.38
2	5.00	0.1 M	− 1.98	− 2.38
3	4.70	0.1 M	− 1.98	− 2.38
4	7.03	0.2 M	− 1.97	− 2.37

From Fig. 3b it is clear that the halfwave potential (with ref. to sat. cal. elect.) equals − 2.38 volts (with $\log \frac{i}{I-i} = 0$). In Table 2 are given the data on polarographic measurements of solutions of pure styrene at different concentrations.

It is clear from Table 2 that the halfwave potential of styrene is independent of the styrene concentration.

Utilizing Fig. 3b and the equation of the wave, we may calculate the apparent number (n) of electrons taking part in the reduction of one molecule of styrene:

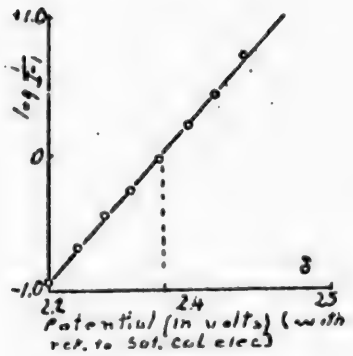


Fig. 3b. Relationship between $\log \frac{i}{I-i}$ and the potential of the mercury dropping electrode (with ref. to sat. cal. elec.) for the styrene wave, based on the polarogram in Fig. 3a.

$$E = E_{1/2} - \frac{0.0596}{n} \log \frac{i}{I-i}; \qquad (1)$$

$$tg\alpha = \frac{\Delta E}{\Delta \log \frac{i}{I-i}} = \frac{2.47 - 2.38}{1.0 - 0.0} =$$

$$= \frac{0.09}{1.0} = 0.09;$$

$$n = \frac{0.0596}{tg\,\alpha} = \frac{0.0596}{0.09} = 0.67.$$

As the value n calculated from formula 1, the number of electrons taking part in the reduction of a molecule of styrene, is a fraction less than one (whereas, theoretically, the reversible process requires $n = 2$), we may draw the conclusion that the reduction of styrene on a mercury dropping electrode is irreversible.

The actual number of electrons taking part in the electrode process can be determined from Ilkovich's equation as applied to the experimental data of Table 1:

$$I = 605 \cdot n \cdot D^{1/2} \cdot m^{2/3} \cdot \tau^{1/6} \cdot c.$$

In this equation, all the values are known from experiment, outside of the coefficient of diffusion; c is the concentration of styrene, equal to 10.35mmol/l; m is the mass of mercury flowing from the capillary per second, equal to 0.17 mg/sec; τ is the period of dropping, equal to 5.6 sec at − 2.1 volts (with ref. to mercury at bottom); I is the limiting diffusion current, equal to 12.6μ A.

As is known [4], the value $605\ n \cdot D^{1/2}$ has been called the constant of the diffusion current. It can be found from Ilkovich's equation by means of the formula:

$$I_D = \frac{I}{L \cdot C},$$

where $L = m^{2/3} \cdot \tau^{1/6} = 0.413\ mg^{2/3}\ sec.^{-1/2}$ is a characteristic of the capillary at − 2.1 volts (with respect to the mercury on the bottom).

Therefore:

$$I_D = \frac{12.6}{0.413 \cdot 10.35} = 2.95.$$

Thus the constant of the diffusion current for styrene during its polarographic investigation in 0.2 M $(C_4H_9)_4NI$ at 25° equals 2.95.

For spherical molecules, the diffusion coefficient can be calculated from the formula [3]:

$$D = \frac{3.32 \cdot 10^{-5}}{v_m^{1/3}}\ cm^2\ sec.^{-1}$$

where v_m is the molecular volume of the substance being investigated:

$$v_m = \frac{M}{d} = \frac{104}{0.908} = 114.5 \ \text{cm}^3/\text{mole}.$$

(M is the molecular weight of the styrene, equal to 104; d is the specific gravity of the styrene, equal to 0.908 g/ml at 20°).

Substituting these values in the equation for the diffusion coefficient, we obtain:

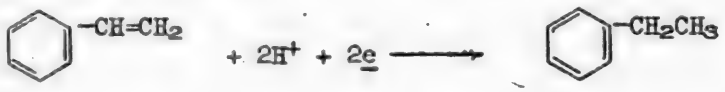
$$D = \frac{3.32 \cdot 10^{-5}}{(114.5)^{1/3}} = \frac{3.32 \cdot 10^{-5}}{4.86} = 0.68 \cdot 10^{-5} \ \text{cm}^2 \cdot \text{sec}^{-1}.$$

As $I_D = 605 \cdot n \cdot D^{1/2}$, then, solving this equation for n, we can determine the number of electrons taking part in the electrode reaction:

$$n = \frac{I_D}{605\, D^{1/2}} = \frac{2.95}{605(0.68 \cdot 10^{-5})^{1/2}} = \frac{2.95}{0.605 \cdot 2.62} = 1.86 \cong 2.$$

The value obtained for n shows that in the electrode reaction 2 electrons take part in the reduction of the styrene.

Consequently, the reduction of styrene takes place according to the following scheme to give ethyl benzene:



Knowing the number of electrons which take part in the reaction, we can use Ilkovich's equation to make a more accurate calculation of the diffusion coefficient of styrene at 25° in 0.2 M tetrabutylammonium iodide:

$$D = \left(\frac{I_D}{605\, n}\right)^2 = \left(\frac{2.95}{605.2}\right)^2 = \left(\frac{2.95}{1.21} \cdot 10^{-3}\right)^2 = 0.60 \cdot 10^{-5} \ \text{cm}^2 \cdot \text{sec.}^{-1}.$$

Further on, we shall cast some light on the proportionality between the height of the styrene wave, and the styrene concentration in the solution.

To construct a calibrated straight line, we prepared a number of solutions of styrene, in which the concentration of the other substances was constant, while the concentration of the reducing substance (styrene) varied. For this purpose, the initial solution of styrene (2 drops in 1 ml 75% alcohol) was added gradually by drops to 1 ml of the electrolyte (0.2 M tetrabutylammonium iodide in 75% alcohol), and the height of the wave measured each time with potentials − 1.7 and − 2.1 volts (with respect to the mercury on the bottom).

From the wave heights measured in this experiment, the residual current was calculated, and the value found for the diffusion current recalculated to microamperes. The concentration of styrene in the electrolyte (in millimoles per liter) was calculated from the formula:

$$c = \frac{d}{M} \cdot \frac{P_1}{d + P_1} \cdot \frac{\Sigma P_2}{d + \Sigma P_2} \cdot 10^6,$$

where d is the specific gravity of 75% ethyl alcohol, equal to 0.871 g/cm³ (at 20°); M = 104, the molecular weight of styrene; P_1 is the weight of two drops of styrene (in the initial solution of the styrene); ΣP_2 is the total weight of the drops of the initial solution of styrene added to 1 ml of electrolyte.

Three series of such experiments in three different electrolytes are given in Table 3. From the data of Table 3, the graph (Fig. 4) was constructed, giving the relationship between the height of the styrene wave in microamperes and the concentration of the styrene in millimoles per liter (calibrated curve).

From Table 3 and Fig. 4 it is clear that there is a direct proportionality between the height of the styrene wave and the concentration of styrene (in the interval of concentration from 1.0 to 30.0mmole/l of styrene).

This is the essential fact in relation to the question of using the polarograph for the quantitative determination of styrene.

We must note that at such negative potentials as − 2.0 and − 2.4 volts (with respect to sat. cal. elec.) which are needed during the polarographic investigation of styrene, we happened to encounter several complicating phenomena connected with the great lowering of surface tension in the mercury drops. This leads to a decided decrease in the dropping period, as well as to a certain variability of this period, and in consequence, to a periodic deviation of the mean point of oscillation on the scale from its normal position. In order to eliminate this difficulty, we carried out experiments on the addition to the solution under investigation of surface-active substances, which, it is well known, help in obtaining more stable and reproducible results. However, it appeared that gelatin and agar themselves had a reducing action at these potentials, and the addition of thymol and methyl red showed no perceptible influence.

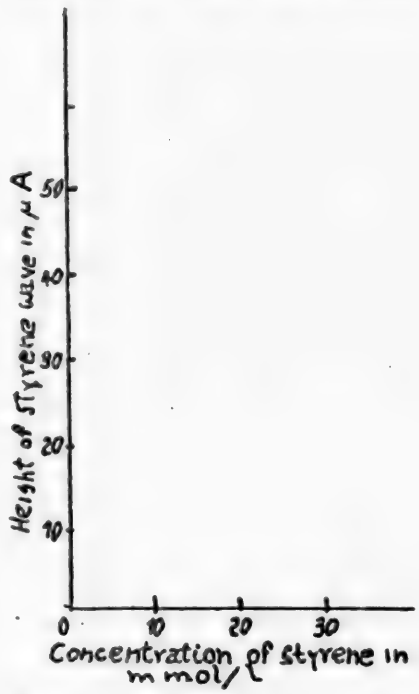


Fig. 4. Relationship between height of styrene wave and styrene concentration in solution containing 0.2 M tetrabutylammonium iodide in 75% ethyl alcohol.

Considerable improvement was found when we used capillaries with a long dropping period (10 to 20 seconds without polarization, and 3 to 5 seconds with a polarization of − 2.4 volts). As a result, the stability of the styrene diffusion current was greatly improved.

We must further note that from 40 to 60 minutes after the beginning of the experiment, we observed the formation of a small flocculent precipitate. A test of the constancy of the height of the styrene wave with time showed that this appearance of a precipitate had no influence on the height of the styrene wave. In addition, special experiments showed that the appearance of this precipitate also took place in a test tube with 0.2 M tetrabutylammonium iodide in the absence of styrene and in the presence of mercury at the bottom. In the absence of mercury no precipitate was formed. Thus, this precipitate was, apparently, a product of the action of mercury upon tetrabutylammonium iodide.

However, from the analytical point of view, the formation of this precipitate cannot hinder the polarographic determination of styrene, as the polarographic measurements on the solution take 10 to 15 minutes, and consequently, are concluded before the precipitate is formed. In addition, as we have said above, the formation of the precipitate exercises no influence on the height of the styrene wave.

The height of the negative potential of the styrene halfwave − 2.38 volts (with respect to sat. cal. elec.) indicates the great difficulty of reducing this

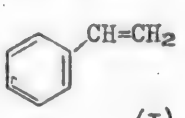
TABLE 3

No. of series of expt.	Styrene concentration, (mmole/l)	Height of styrene wave (A)	Constant of diffusion current	Deviation of constant of diffusion current from average value	Capillary characteristic at − 2.1 volts (with ref. to Hg at bottom)($mg^{2/3}$ $sec.^{-1/2}$)
1	1.00	3.6	3.03	-0.01	1.20
	3.06	11.9	3.24	+0.20	
	4.10	16.1	3.26	+0.22	
	5.58	19.8	2.96	-0.06	
	5.90	21.7	3.06	+0.02	
	6.98	25.5	3.03	-0.01	
	8.00	29.8	3.10	+0.06	
2	3.77	8.05	3.56	+0.52	0.60
	9.25	14.8	2.66	-0.38	
	17.5	30.7	2.92	-0.12	
	21.5	38.0	2.95	-0.09	
	24.8	45.5	3.08	+0.04	
	28.6	52.4	3.06	+0.02	
3	7.21	12.86	2.98	-0.06	0.60
	10.9	19.96	3.06	+0.02	
	14.2	24.57	2.90	-0.14	
	17.7	30.91	2.90	-0.14	
	Average value.....		3.04		

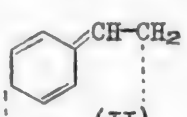
hydrocarbon with the mercury dropping electrode. It appeared to us that this difficulty could to some degree be explained by means of the theory of resonance.

The theory of resonance permits us to explain certain peculiarities of compounds with conjugated double bonds. The styrene molecule can be regarded as a system in which the double bond of the side chain is conjugated with the double bonds of the ring. This results in delocalization of the π-electrons and the appearance of resonance energy equal to 7 kilocalories [5].

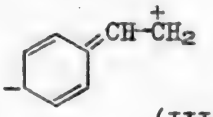
Styrene can have the following 3 basic structures:



(I)



(II)



(III)

The presence of a dipole moment (0.37D) in styrene also confirms the presence of an ionized structure (III).

It is known that resonance, determined by the delocalization of the electrons, finally results in the increased stability of the molecule, and lowers the energy of the system.

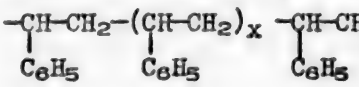
In addition, the specific effect of the Dewar structure (whose energy is much greater than that of the Kekule structure) is very insignificant in the styrene molecule.

The presence of resonance in the styrene molecule, and, in connection with this the superposition of simple and double bonds in the side chain, permits us to explain not only the overall decrease in the energy of the system, but also the difficulty in reducing styrene on the mercury dropping electrode.

It is known from the data in the literature [1] that substituted styrenes particularly β-methylstyrene, are reduced on the mercury dropping electrode with even more difficulty (at -2.54 volts). It is obvious that the introduction of the CH_3 group into the molecule of styrene atabilizes the double bond. This permits us to draw the very important practical conclusion that styrene can be determined polarographically in the presence of its homologs.

Polarographic Investigation of Polystyrene

The initial solution in xylene had a polystyrene concentration of about 200 mmole/l (basing the calculation on the molecular weight of unpolymerized styrene). A few drops of this solution were added to the electrolyte, 0.2 M tetrabutylammonium iodide in 75% alcohol, and the solution measured polarographically. The final concentration of polystyrene in the solution was about 5 mmole/l (calculated as styrene). During the measurements at potentials of -2.1 and -1.7 volts, only a very small wave of about 0.3 μA was observed instead of 10.0 μA, as for unpolymerized styrene at the same concentration. This almost complete fading away of the wave in polystyrene solution can, apparently, be explained by the large number of double bonds used up in forming the polymer molecules,[6].



Double bonds can remain, obviously, only at the ends of these polymer molecules. It is this, apparently, that is responsible for the almost complete absence of a wave in the polystyrene solution.

The experimental data we obtained show the possibility of using a polarographic method for the investigation of the process of polymerization of styrene. The decrease in the styrene wave directly indicates the amount of polymerized styrene.

SUMMARY

1. It has been shown that in a 0.2 M solution of tetrabutylammonium iodide in 75% ethyl alcohol, styrene gives a well-expressed polarization wave.

2. The polarographic characteristic of the styrene wave in 0.2 M $(C_4H_9)_4NI$ in 75% ethyl alcohol, has been obtained. It has been shown that the process of reduction of the styrene on the mercury dropping electrode is irreversible, and that two electrons take part in the electrode process.

3. A proportionality has been found between the height of the styrene wave and the concentration of styrene in solution, in the interval of concentration from 1.0 to 30.3 millimole/l of styrene. This permits us to draw the conclusion that this styrene wave is entirely suitable for the polarographic determination of styrene.

4. It has been found that the wave is almost completely extinguished in polystyrene.

5. The reduction of styrene on the mercury electrode has been discussed from the point of view of the theory of resonance.

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THE SOLUBILITY OF OXYGEN IN SEVERAL ORGANIC LIQUIDS

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The present work consisted of an investigation of the solubility of oxygen in cracked gasoline, xylol, ligroin, toluene, and white spirit at room temperature and atmospheric pressure; in addition the influence of temperature upon the solubility of oxygen in xylol was investigated.

To determine the solubility, we constructed an apparatus schematically depicted in Fig. 1. Its chief characteristic was that a preliminary degasification of the solvent could be carried out in the same apparatus, and the degasified solvent saturated in an absorption vessel under the pressure of its vapors; thus the possibility of contact with air was excluded. A second peculiarity of the apparatus was that all the means of passage of the solvent, including capillaries which joined the gas burette to the absorption flask, were made of glass. The absence of stoppers made of rubber compounds in the path of the solvent excluded the possibility of the latter's contamination with substances extracted from the rubber.

A glass capillary guaranteed against errors connected with the absorption of oxygen by rubber, or swelling due to the vapors of the solvent as happens when rubber is used to obtain a flexible joint of the burette with the absorption flask.

The possibility of constructing the apparatus of glass throughout permitted degasification and the determination of solubility in a single apparatus, as well as the use of an electromagnetic agitator for the necessary mixing of the solvent.

The apparatus consists of an absorption flask, 18, in the form of a glass cylinder of measured capacity, at the bottom of which lies the magnet 23, sealed in a glass tube, belonging to the electromagnetic agitator, 24. Upon turning on the motor, the agitator magnet 23 begins to revolve with a velocity of 120 rev./min. providing energetic shaking of the liquid in the absorption flask, which is held in the thermostat 25. The thermostat is a glass beaker with an aperture for the passage of tube 26.

The thermostat liquid is poured into the tube; it is chosen so that its boiling point corresponds to the temperature of the experiment. The beaker 25 is covered with an ebonite cap with openings for the thermometer 28 and the reflux condenser, 29. The thermostat is heated by the electric heater, 30. The absorption flask is joined by means of capillary 19 to the gas burette 31.

The essential condition which determines the sensitivity of the apparatus is the ratio of the dimensions of the absorption flask and the gas burette, which must be chosen according to the value of the solubility of the gas in the liquid. In our apparatus, the volume of the absorption flask amounted to 175 ml, that of

the gas burette to 100 ml at a height of 100 cm. The burette is graduated in tenths of a milliliter. This ratio of dimensions gave satisfactory accuracy of measurement in all cases.

The absorption flask is united by means of a glass tube to flasks 1 and 2, which serve for preliminary degasification of the solvent. The method of determining the solubility in the apparatus described is comprised in the following operations. The degasification flasks are filled to 3/4 of their volume with the liquid being investigated through the adapter of the reflux condenser, 3, which is then joined to the vacuum line. The 3 way stopper 5 is turned into such a position that both degasification flasks are connected with the reflux condenser. When the vacuum is turned on, the solvent in the flasks begins to boil; this is permitted to continue for 25 to 30 minutes, and the solvent is then cooled under vacuum to the temperature of the experiment. Then, under the combined action of the vacuum, applied to the absorption vessel, and the vapor pressure of the solvent, which again begins to boil in flask 2, the degasified solvent is drawn from flask 1 to the absorption vessel. The latter is filled up to the stopcock 17, which is then turned off. The following operations include filling the gas burette 31, and the capillary 19, with oxygen, after which the initial conditions of the experiments are measured: temperature of the burette and thermostat, barometric pressure, initial volume of gas in the gas burette. Then the gas burette is joined to the absorption vessel. Simultaneously with the raising of the equalizer 32, 25 ml of the solvent is forced from the absorption flask into the graduated cylinder through the extended end of the tube 22, and then the stopcock 20 is turned, and the electromagnetic agitator is started.

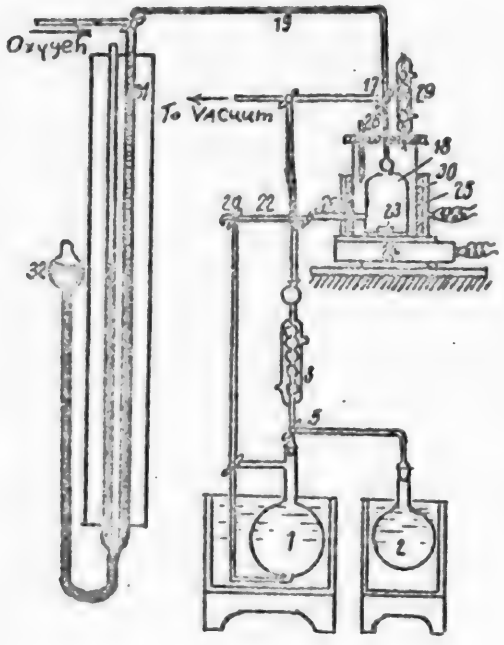

Fig. 1. Apparatus for the determination of the solubility of oxygen in organic liquids.

Solution takes place at constant pressure, equal to atmospheric; this is controlled by raising the equalizer as the levels in the burettes change. The end of the rise of the mercury level in the gas burette shows that the process of solution has been completed. The length of the experiment is 30 to 40 minutes; after the conclusion of the process, the final conditions are measured.

The calculation is carried out according to Ostwald's formula [1].

$$\underline{1}_A^T = \frac{(v_1 - v_2)\,\frac{H - P_B^T}{H - P_A^T} \cdot \frac{T_A}{T_B} - \Delta v}{v_{fl}}$$

where: l_A^T is the solubility in ml of the gas in 1 ml of liquid at atmospheric pressure and the temperature of the experiment;

v_1 is the initial volume of gas in the burette;

v_2 is the final volume of gas in the burette;

H is the external pressure (in mm of mercury column);

P_A^T is the partial pressure of the vapor of the solvent at the temperature of the burette;

P_B^T is the partial pressure of the vapor of the solvent at the temperature of the thermostat;

T_A is the absolute temperature of the thermostat;

T_B is the absolute temperature of the burette;

Δv is the volume filled with gas in the absorption vessel, equal to the volume of liquid displaced;

v_{fl} is the volume of liquid in the absorption vessel.

In Table 1 are given the results of the determination of the solubility of oxygen in the liquids investigated, at room temperature.

TABLE 1
Solubility of oxygen in organic liquids

Solvent	Temperature of expt. °	Solubility of oxygen (ml oxygen per 1 ml solvent)*
Technical xylol (range 134-138°)	23	0.177
Toluene.....	20	0.128
Ligroin (110-120°).....	20	0.156
White spirit (165-200°).....	19	0.170
Cracked gasoline (115-150°).....	19	0.178

TABLE 2
Solubility of oxygen in xylol at different temperatures

Expt. No.	Temp. °	Solubility (ml oxygen in ml solvent)	Absorption coefficient (ml oxygen at normal conditions in ml solvent)
1	23	0.177	0.162
2	80	0.226	0.179
3	100	0.268	0.192

In Table 2 are given the results of a determination of the solubility of oxygen and the absorption coefficient in xylol at temperatures of 20, 80, and 100°.

Fig. 2 shows the relation between temperature and the absorption coefficient of oxygen in xylol. As can be seen, the solution of the oxygen in xylol has a positive temperature coefficient. This is of some theoretical interest, being an additional confirmation of the fact that the temperature coefficient of the solubility of gases of the type O_2, N_2, and H_2 is positive.

There is an attempt at a thermodynamic explanation of the phenomenon in the work of Amerongen [2], who in his turn cites the work of Khorint.

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*The figures given are averages for three or four experiments. The differences between parallel experiments did not exceed ±0.001.

Having ascertained that a positive temperature coefficient is observed only in those cases where the absolute value of the solubility is small, the authors show the connection between solubility and thermal effect, assuming that the latter is completely determined by the work of solution. From this they find that the value for the solubility of $l_A^T = 1.0$ is critical. At a solubility greater than the critical, a negative value of the temperature coefficient is to be expected; at a solubility less than the critical, the temperature coefficient will become positive.

The conclusion of the authors, however, raises some doubt because of the fact that they did not take into account the work of external forces during the change in the total volume of the system.

We suggest the following thermodynamic interpretation of the phenomenon: in the general case of equilibrium of a two-component system in two phases, we have, as an expression of the dependence upon the temperature of the equilibrium constant K:

$$\frac{\partial \log K}{\partial T} = \frac{\partial \log l_A^T}{\partial T} = -\frac{Q}{RT^2}, \qquad (1)$$

where l_A^T is the solubility of the gas, i.e., $\frac{v_{gas}}{v_{liq}}$, and Q is the heat of solution.

In place of Q, considering the process of isothermal solution of one mole of gas under the constant pressure of one atmosphere, we have:

$$Q = \Delta U + P\Delta v = \Delta U + RT. \qquad (2)$$

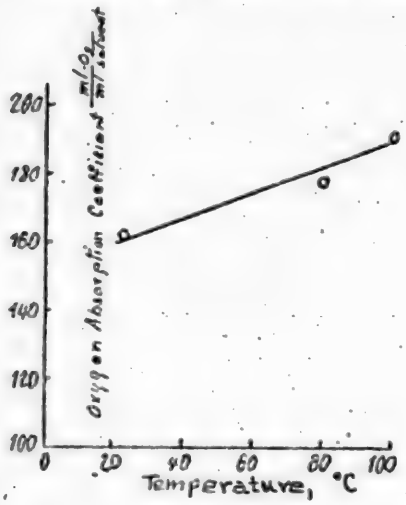

Fig. 2. The relation between the absorption coefficient of oxygen in xylene and the temperature.

To a first approximation, the change in the internal energy of the system will be given correctly if we neglect the heat of reaction between the molecules of gas and the molecules of liquid; it is determined by the work expended on the isothermal process of transferring a mole of gas from the initial volume v_{gas} to the final volume of gas in the solvent, which is approximately equal to v_{liq}.:

$$\Delta U \cong -RT \ln \frac{v_{liq}}{v_{gas}} = RT \ln l_A^T \qquad (3)$$

Thus, we have:

$$Q = RT \ln l_A^T + RT \quad \text{or} \quad Q = RT(\ln l_A^T + 1),$$

whence $Q = 0$ when $\ln l_A^T = -1$ and $l_A^T = \frac{1}{e} \approx 0.37$.

When $l_A^T > 0.37$ $Q > 0$ and the temperature coefficient of solubility determined by (1) is negative.

When $l_A^T < 0.37$ $Q < 0$, and the temperature coefficient of solubility must be positive.

Thus, the positive temperature coefficient of solubility, as a consequence of the latter, does not exceed 0.37, on thermodynamic grounds.

The deviations which take place are apparently explicable by the fact that the heat of reaction between the molecules of gas and solvent is not always negligible.

SUMMARY

1. An apparatus has been described for the determination of the solubility of gases in organic liquids.

2. The solubility of oxygen has been determined in gasoline, xylol, ligroin, and white spirit at temperatures from 19 to 23°.

3. It has been found that the solubility of oxygen in xylol in the temperature interval from 23-100° increases linearly with a rise in the temperature.

4. It has been shown from thermodynamic considerations that a positive temperature coefficient of solubility of a gas may be found when the solubility of the gas in the range of temperature investigated does not exceed 0.37.

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DIENE SYNTHESES WITH PIPERYLENE

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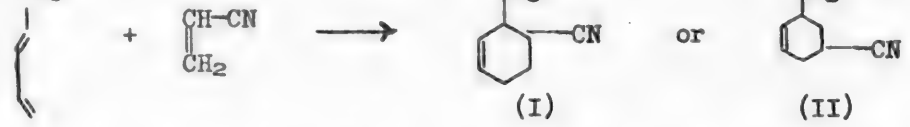
Piperylene has of late begun to receive considerable attention. It is one of the most accessible dienes, existing in the cis and trans forms [1].

The diene synthesis with piperylene has been of frequent service as a method of investigation [2]. The diene synthesis takes place only with the trans form [3] and theoretically can give two isomeric products because of the possibility of addition of dieneophil compounds in two directions.

One of us earlier investigated the diene synthesis with acrolein [4] and several other dieneophils. However, the manner of addition of the asymmetrically constructed dieneophil to piperylene was not shown. At the same time, the question of the orienting influence of groups upon the diene synthesis is of great interest from the point of view of its interpretation by means of electronic considerations. These induced us to undertake an investigation of the diene synthesis with piperylene and asymmetrically constructed dieneophils, and to determine the manner of their addition. At the time this investigation was concluded, a communication on a similar theme appeared in print. At the end of 1947 there was published a paper by Frank, Emmick, and Johnson [5] which described the diene synthesis of piperylene with the nitrile of acrylic acid, and in 1948 one by A.A.Petrov and Sapozhnikova [6] described the same synthesis of piperylene with acrylonitrile.

The results of our investigations are in accord with the conclusions of these authors, but the materials for the diene synthesis with piperylene are not limited to the nitrile of acrylic acid, and the method of showing the structure of the products of the diene synthesis is somewhat different from that in the works cited; this induced us to publish the present communication.

As a result of the diene synthesis of piperylene with acrylic nitrile, we may expect the formation of 2-methyl-1,2,5-6-tetrahydro benzonitrile (I), or 3-methyl-1,2,3,6-tetrahydro benzonitrile (II), or mixture of the two isomers:



(I) (II)

Frank, Emmick, and Johnson, on the basis of the dehydrogenation of the addition product of acrylonitrile and trans-piperylene with sulfur, and the saponification of the toluic nitrile obtained, arrived at the conclusion that the chief product of the reaction of piperylene with acrylonitrile was the nitrile (I), along with small quantities of the nitrile (II), as saponification of the toluene nitrile obtained gave o- and m-toluic acids in the ratio 7:1.

A.A.Petrov and A.F.Sapozhnikova, working with piperylene which contained about 50% of the trans form, obtained 46% of condensation product, and showed that the cis-form did not enter into reaction with the acrylonitrile at 130-135°.

At 180° condensation took place as a result of the obvious change of part of the cis-form to the trans. During the saponification of the nitrile obtained, A.A. Petrov and A.F.Sapozhnikova obtained a liquid acid with b.p. 138° at 20 mm. This led them to the conclusion that it was 2-methylcyclohexene-3-carboxylic acid, and that the product of addition of the acrylonitrile to piperylene had the structure (I). By saponification of the amide obtained from the nitrile, A.A.Petrov and A.F. Sapozhnikova obtained a crystalline acid with the same b.p. Petrov and Sapozhnikova considered the acids they had obtained to be cis and trans isomers. In their opinion addition of the acrylonitrile to piperylene at 135° gave 50% cis, 50% trans form.

A.A.Petrov and A.F.Sapozhnikovaassert that this manner of addition of acrylonitrile to piperylene is in accord with the requirements of electron theory.

We heated the nitrile of acrylic acid with piperylene at 130-140° for 24 hours, and obtained an addition product in 64% yield. It had the following constants:

B.p. 73-74° at 8 mm; n_D^{20} 1.4683; d_4^{20} 0.9289; MR_D 36.28.
$C_8H_{11}N_2|^=$. Calculated: MR_D 36.29.

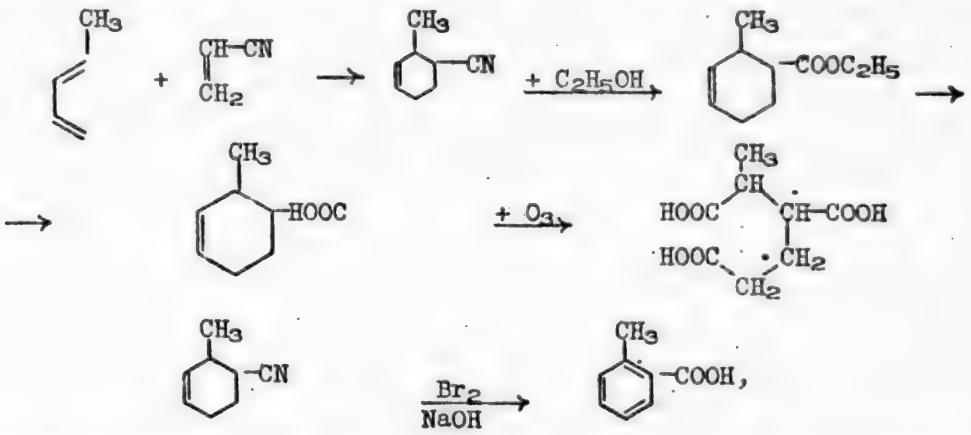
These constants are close to those of Frank, Emmick and Johnson (b.p. 72-74° at 9 mm; n_D^{20} 1.4682) and of A.A.Petrov and A.F.Sapozhnikova (b.p. 89.5-90° at 20 mm; n_D^{20} 1.4700; d_4^{20} 0.9307; MR_D 36.3). The structure of the product we had obtained was shown in the following manner: the nitrile was converted into the ethyl ester by the action of alcohol in the presence of hydrogen chloride. It had the following constants:

B.p. 138-140° at 100 mm; n_D^{20} 1.4619; d_4^{20} 0.9741; MR_D 47.40.
$C_{10}H_{16}O_2|^=$. Calculated: MR_D 47.37.

Upon saponification of the ester with soda, the acid was obtained, with

B.p. 138-140° at 20 mm; n_D^{20} 1.4738; d_4^{20} 1.0397; MR_D 37.87.
$C_8H_{12}O_2|^=$. Calculated: MR_D 38.01.

Ozonification of the acid in soda solution gave pentanetricarboxylic acid-1,3,4, with m.p. 176-178°, which had been described by Perkin [7]. Dehydrogenation of the nitrile with bromine, according to the method of Einhorn and Willstätter [8], followed by the hydrolysis of the nitrile, gave o-toluic acid, with m.p. 103-104° [9]. The course of the reactions, which could be represented in the following manner:



left no doubt about the structure of the addition product. We isolated no derivatives that indicated the presence of the isomeric nitrile (II).

Earlier, B.A.Arbuzov and E.Fink [4] obtained an addition product from

acrolein and piperylene. Its structure, in the sense of the orientation of the acrolein during the addition, was not determined. We repeated the experiments on the addition of acrolein to piperylene and showed the structure of the addition product.

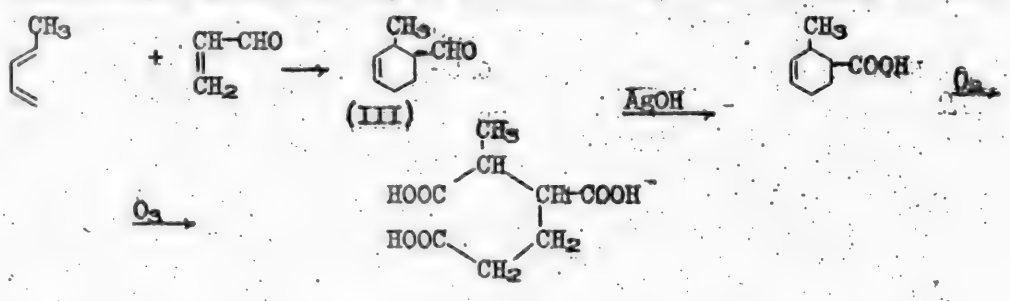
An aldehyde was obtained in 56% yield, with the following constants:

B.p. 56-58° at 11 mm; n_D^{20} 1.4653; d_4^{20} 0.9435; MR_D 36.35.
$C_8H_{12}O$. Calculated: MR_D 36.48.
The aldehyde gave a semicarbazone with m.p. 167-168°.

To determine the structure of the addition product, it was oxidized with moist silver oxide to give the corresponding acid. There was thus obtained in 89% yield 2-methyl-Δ^3-cyclohexene-1-carboxylic acid, with m.p. 52-52.5° [a].

As was shown by A.A.Petrov, saponification of the crystalline amide obtained by the partial hydrolysis of the nitrile from piperylene and acrylonitrile gave an acid with m.p. 53°, corresponding to the trans form. By means of the acid chloride of the acid with m.p. 52-52.5°, we obtained an amide of the acid with m.p. 157-158°, in close agreement with the value of the amide A.A.Petrov had obtained from the nitrile (m.p. 159-160°). Upon ozonolysis of the acid with m.p. 52-52.5°, we obtained an acid with m.p. 177°, identical with the pentanetricarboxylic acid-1,3,4 we had earlier obtained from the liquid 2-methyl-Δ^3-cyclohexane aldehyde-1 (mixed test).

The data given above leave no doubt that the addition product of the acrolein to piperylene has the structure trans-2-methyl-^{3}-cyclohexane aldehyde-1 (III). The course of the addition reaction and of the reactions which show the structure of the aldehyde obtained, may be represented by the following scheme:



It is of interest to note that in the case of the acrolein-piperylene addition product, we observed no liquid cis-acid during the oxidation of the aldehyde.

Alder and Rickert [10] showed that butadiene and several other dienes enter into an addition reaction with alkylidene- and benzylidenemalonic and acetoacetic esters. Alder and Rickert carried out the reaction only with butadiene, 2,3-dimethyl butadiene, and cyclopentadiene, where the assymetry of the dieneophil could give only a single addition product.

We carried out experiments on the addition of alkylidene- and benzylidenemalonic and acetoacetic esters and determined the structure of the products obtained.

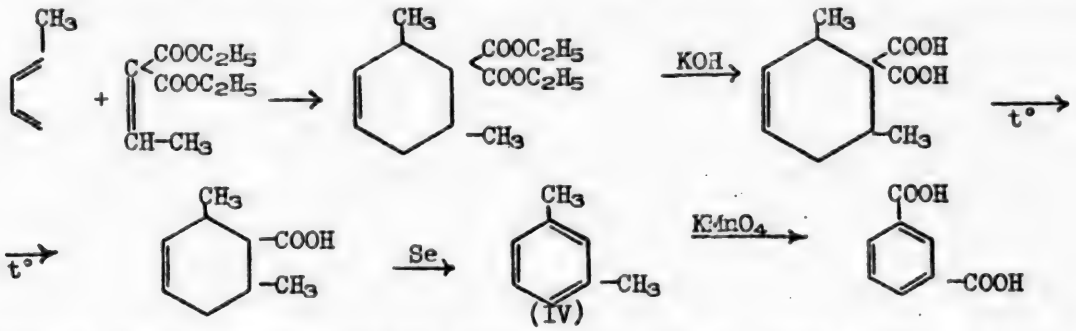
By the action of ethylidenemalonic ester on piperylene at 170-175°, we obtained in 74% yield a product with the constants:

B.p. 123-124° at 5 mm, 136-138° at 11 mm; n_D^{20} 1.4619; d_4^{20} 1.0416; MR_D 67.07.
$C_{14}H_{22}O_4$. Calculated MR_D 67.49.

This indicated, as was made clear by investigation, that the compound was the diethyl ester of 2,6-dimethyl-Δ^3-cyclohexene dicarboxylic acid-1,1 (IV). Its structure was shown by the following reactions. Saponification of the ester gave a dibasic acid with m.p. 188° (decomp); upon heating to 200°, this went over into

a monobasic acid with m.p. 55-56°. Dehydration of this latter acid with selenium at 360° gave m-xylene, which was identified by its oxidation to isophthalic acid with m.p. 341-343°.

The course of the reactions indicated can be shown by the following scheme:



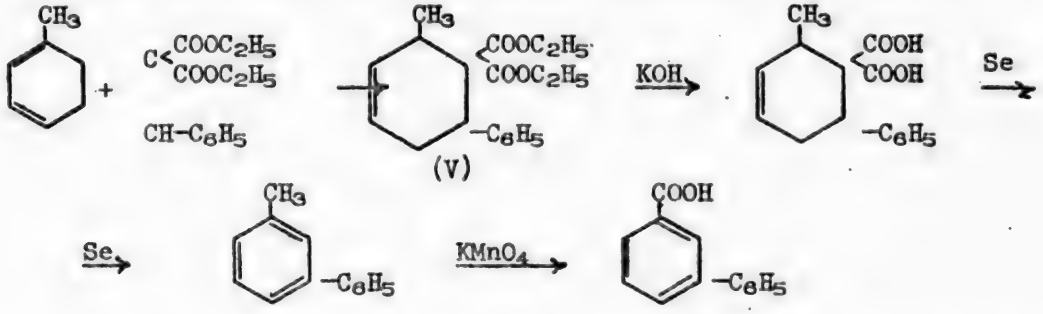
The reaction between piperylene and benzalmalonic ester takes place in a similar manner.

Heating of the piperylene with benzalmalonic ester at 190° gave an addition product (yield of pure product 39.3%) with the following constants:

B.p. 170-172° at 4 mm; n_D^{20} 1.5206; d_4^{20} 1.1006; MR_D 87.40.

$C_{19}H_{24}O_4$ |=4. Calculated MR_D: 86.99.

It proved to be the diethyl ester of 2-methyl-6-phenyl-Δ^3-cyclohexenedicarboxylic acid-1,1 (V), whose structure was shown by the following reactions:



The dibasic acid has M.p. 183° (with decomp.). The m-phenyltoluene was not isolated in pure form, but was directly oxidized to give m-phenylbenzoic acid with m.p. 159-161° (m.p. of m-phenylbenzoic acid 162° [11])

On heating with piperylene to 180°, ethylideneacetoacetic ester gave an addition product in 74% yield, based on the ethylideneacetoacetic ester, with constants:

B.p. 116-118° at 5 mm; n_D^{20} 1.4724; d_4^{20} 1.0326; MR_D 60.97.

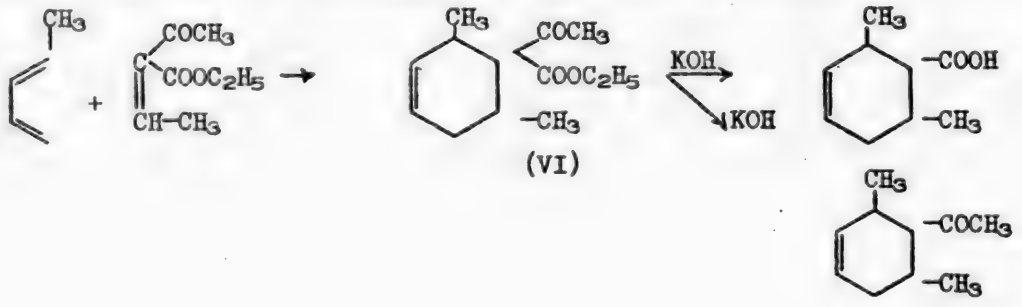
$C_{13}H_{20}O_3$ |=. Calculated: MR_D 61.23.

An investigation of its chemical properties showed that it was the ethyl ester of 2,6-dimethyl-1-acetyl-Δ^3-cyclohexenecarboxylic acid-1 (VI). Saponification with alkali followed by acidification gave an acid with m.p. 56°, which was identical with the 2,6-dimethyl-Δ^3-cyclohexene-1-carboxylic acid (m.p. 55°) obtained earlier by the saponification and splitting off of CO_2 from the addition product of ethylidenemalonic ester and piperylene. The formation of the 2,6-dimethyl-^{3}-cyclohexene-1-carboxylic acid proved the structure of the addition product.

In addition to the acid, as a result of the ketonic cleavage of the addition product, we isolated in 45% yield a ketone which gave a semicarbazone with m.p. 124°, and had the following constants:

B.p. 80-81° at 12 mm; n_D^{20} 1.4635; d_4^{20} 0.9259; MR_D 45.33.
$C_{10}H_{18}O$ |=. Calculated: MR_D 45.72.

Judging from the structure of the initial addition product (VI), the ketone must have the structure (VII) 2,6-dimethyl-1-acetyl-Δ^3-cyclohexene. The reactions described can be represented in the following manner:



(VI)

(VII)

In all the cases described of the addition to piperylene of the alkylidene and benzylidenemalonic and alkylideneacetoacetic esters, we did not succeed in observing any products of addition in the reverse manner.

An investigation of the reaction between benzalacetoacetic ester and piperylene showed without any doubt that in this case the reaction took place in both directions.

Heating of the piperylene with benzalacetoacetic ester at 180° gave products from which two fractions could be isolated, with the following constants:

1) 9.3 g; b.p. 165-167° at 4 mm; n_D^{20} 1.5288; d_4^{20} 1.0980; MR_D 80.41. $C_{18}H_{22}O_3$ |=$_4$. Calculated MR_D 80.72.

2) 5 g; b.p. 167-171° at 4 mm; n_D^{20} 1.5300.

The second fraction began to crystallize after a month. After recrystallization from methyl alcohol, the crystals had m.p. 61° (4.3 g). Saponification of the first fraction with aqueous-alcoholic alkali gave a neutral portion, insoluble in the water-alcohol solution (27%), and an acid part, separated after acidification of the aqueous-alcoholic layer (53%).

The acid, separated from the salt, had b.p. 160-170° at 5 mm, and did not crystallize. Upon dehydrogenation with selenium at 360° and oxidation of the dehydrogenation product with potassium permanganate, m-phenylbenzoic acid with m.p. 158-160° (mixed m.p.) was obtained.

The formation of m-phenylbenzoic acid showed that the first fraction consisted of the ester of 2-methyl-6-phenyl-1-acetyl-Δ^3-cyclohexenecarboxylic acid-1 (VIII).

The part insoluble in alkali had:

B.p. 150-156° at 10 mm; n_D^{20} 1.5301.

and was, apparently, 2-methyl-6-phenyl-1-acetyl-Δ^3-cyclohexene.

The second fraction with b.p. 167-171° at 4 mm, upon saponification with a 25% alcohol solution of caustic potash, followed by acidification of the aqueous alkali solution, gave an acid; after some time this began to crystallize, and

after recrystallization from aqueous methyl alcohol had m.p. 83° (yield 70%).

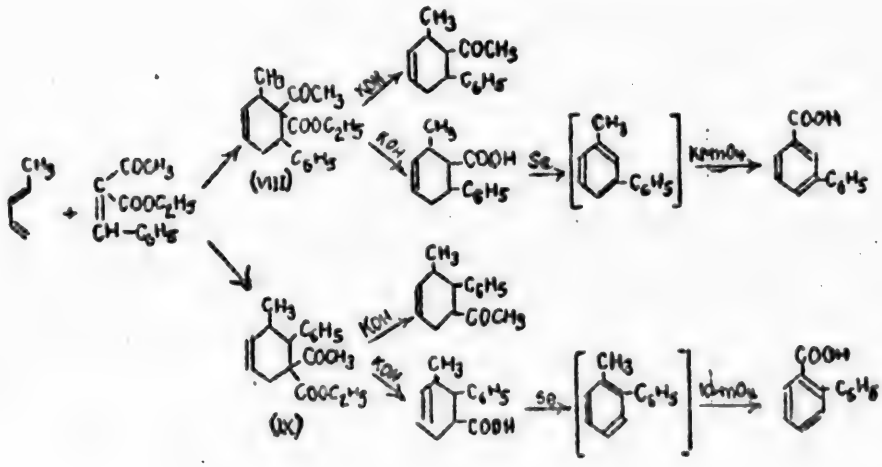
An investigation showed that it was 3-methyl-2-phenyl-Δ^4-cyclohexene-carboxylic acid-1, as dehydrogenation with selenium at 360° and oxidation of the dehydrogenation product with potassium permanganate gave o-phenylbenzoic acid with m.p. 112-113° (data in the literature, m.p. 113.5-114.5° [12]).

In addition to the acid with m.p. 83°, saponification of the fraction with b.p. 167-171° at 4 mm with alcoholic alkali gave a product (0.8 g) insoluble in the water-alcohol layer; this gave a semicarbazone with m.p. 195°.

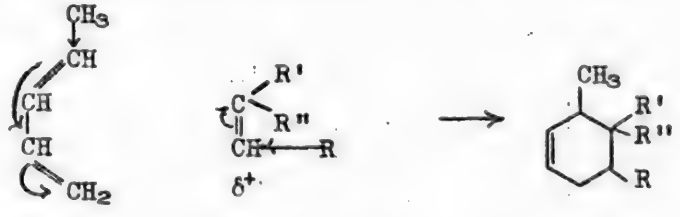
This product is obviously 3-methyl-2-phenyl-1-acetyl-Δ^4 cyclohexene. Further investigation is required to confirm its structure.

Thus, in the addition of benzalacetoacetic ester to piperylene, both possible isomers are formed, as has been shown by the reactions given above.

The course of these reactions can be represented by the following scheme:



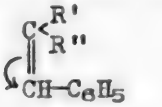
The manner of addition of such dieneophils as the nitrile of acrylic acid, acrolein, and ethylidenemalonic and ethylidenacetoacetic esters, to piperylene is in good accord with the direction of polarization of the piperylene and the dieneophils mentioned [13]



$R' = CN, CHO, COCH_3, COOC_2H_5$;
$R'' = H$ or $COOC_2H_5$.

In the case of those dieneophils where $R = C_6H_5$, as a result of the tendency of the phenyl radical to accept and to give electrons,

in addition to the direction of polarization shown above, the polarization of the dienophile can also take place in the reverse direction:



This direction of polarization can lead to the formation of an isomeric addition product.

In fact, in the case of benzalacetoacetic ester, we showed that in addition to the chief product of reaction, the ethyl ester of 2-methyl-6-phenyl-1-acetyl-Δ^3-cyclohexene carboxylic acid-1 (VIII), there was also formed a large quantity of the isomeric ester 3-methyl--2-phenyl-1-acetyl-Δ^4-cyclohexene carboxylic acid-1, (IX).*

The formation of a small quantity of the isomeric addition product could also be expected in the case of benzalmalonic ester.

We did not succeed in isolating it or proving its presence in the products of the reaction between piperylene and benzalmalonic ester. It is possible that a more careful investigation of the products of reaction of piperylene and benzalmalonic ester after overcoming experimental difficulties would enable us to observe the second addition product as well.

EXPERIMENTAL

The piperylene used for the diene synthesis had the following constants:

B.p. 41-43°; n_D^{20} 1.4258; d_4^{20} 0.6853.

1. Addition of the Nitrile of Acrylic Acid to Piperylene

20 g of piperylene fraction, 16.4 g of acrylonitrile, and 0.1 g of hydroquinone were heated in sealed tubes at 130-140° for 24 hours. Then the contents of the tubes were subjected to vacuum distillation in a Widmer column. There was obtained 24 g of the nitrile of 2-methyl-Δ^3-cyclohexene carboxylic acid, i.e., 64% based on the acrylonitrile:

B.p. 69-70° at 6 mm or 73-74° at 8 mm; n_D^{20} 1.4683; d_4^{20} 0.9289; MR_D 36.28. $C_8H_{11}N$. Calculated MR_D: 36.29.

The nitrile obtained was a colorless, oily liquid with an almond odor.

0.1034 g substance: 0.3011 g CO_2; 0.0840 g H_2O.
Found %: C 79.42; H 9.09.
$C_8H_{11}N$. Calculated %: C 79.29: H 9.15.

No other fraction which might contain an isomeric nitrile was isolated.

a) Alcoholysis of the nitrile. A solution of 20 g of the nitrile in 300 ml of absolute ethyl alcohol was heated with a reflux condenser on the water bath for 8 hours; into the boiling solution was led a rapid stream of dry hydrogen chloride. After 8 hours, the passage of the hydrogen chloride was discontinued and the heating continued for 4 more hours. Then the contents of the flask were poured into 800 ml of water and carefully extracted with ether. After drying of the ether extract and driving off of the ether, the residue was fractionated. There was obtained 11 g (40%) of an oily liquid with an aromatic odor; it was the ethyl ester of 2-methyl-Δ^3-cyclohexene carboxylic acid:

B.p. 95-97° at 15 mm, or 138-140° at 100 mm; n_D^{20} 1.4619; d_4^{20} 0.9741; MR_D 47.40. $C_{10}H_{16}O_2$. Calculated MR_D 47.37.

0.1202 g substance: 0.3139 g CO_2; 0.1043 g H_2O.
Found %: C 71.22; H 9.71.
$C_{10}H_{16}O_2$. Calculated %: C 71.39; H 9.58.

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*Repeated experiments on dehydrogenation of the acid with m.p. 83°, followed by oxidation, showed that the compound with m.p. 112-113° appeared to be not 2-phenylbenzoic acid, but impure 3-phenylbenzoic acid. Thus, the formation of the isomeric adduct (X) was not confirmed.

b) 10 g of the ester obtained was mixed with an aqueous-alcoholic solution of 7 g of soda; the solution obtained was boiled on the water bath for 12 hours, after which the contents of the flask were boiled with several portions of animal charcoal, evaporated to a small volume, and acidified by the addition of sulfuric acid (1:5). They were then carefully extracted with ether.

After removal of the ether, there was obtained 6.1 g (73%) of a thick syrup with an unpleasant odor, b.p. 138-140° at 20 mm; it did not crystallize upon refrigeration.

n_D^{20} 1.4738; d_4^{20} 1.0397; MR_D 37.87.
$C_8H_{12}O_2|^=$. Calculated MR_D: 38.01.

The silver salt was obtained in the form of a white powder.

0.5337 g substance: 0.2318 g Ag.
Found %: Ag 43.44.
$C_8H_{11}O_2Ag$. Calculated %: Ag 43.67.

c) 5 g of the acid obtained was dissolved in 50 ml of soda solution, containing 3 g of soda, and ozonified for 16 hours. The ozonide solution was mixed with snow and oxidized in the cold with 800 ml of a 1% solution of potassium permanganate, while being stirred energetically. At the end of the oxidation, the reaction flask was heated on the water bath for 2 hours. After filtering off the manganese dioxide, the filtrate was concentrated in a vacuum to a small volume, acidified with dilute hydrochloric acid (1:1), and evaporated on the water bath to dryness. The residue was mixed with pure sand and extracted with dry ether. After the removal of the ether, 3.7 g of a solid substance was obtained in the form of white grains, which, after recrystallization from concentrated hydrochloric acid and drying, had m.p. 176-178°; this corresponded to the data of Perkin [7] for pentanetricarboxylic acid-1,3,4.

d) Dehydrogenation of the nitrile. 1.3 g of the nitrile was heated with an accurately calculated quantity of bromine (3.41 g) in a sealed tube at 200° for 2 hours. Then the contents of the tube were boiled with a 30% solution of caustic soda for 16 hours. After this the solution was acidified with dilute hydrochloric acid (1:4). A white precipitate settled out; after recrystallization from dilute alcohol, it had m.p. 103-104°, which corresponded to the data of the literature for o-toluic acid [8].

2. Condensation of Piperylene and Acrolein

60 g of acrolein, 115 g of piperylene, and 0.5 g of hydroquinone were heated in sealed tubes at 125-130° for 8 hours. After removal by distillation of the unreacted components, there was isolated by fractional distillation with a Widmer column 70 g (56% based on the acrolein) of 2-methyl-Δ^3-cyclohexene-aldehyde:

B.p. 56-58° at 11 mm; n_D^{20} 1.4653; d_4^{20} 0.9435; MR_D 36.35.
$C_8H_{12}O|^=$. Calculated MR_D 36.48.

No other fraction, which might contain an isomer, could be separated.

By Zelinsky's method, a semicarbazone was obtained with m.p. 167-168° (from alcohol).

0.1086 g substance: 0.2381 g CO_2; 0.0816 g H_2O.
Found %: C 59.79; H 8.41.
$C_9H_{15}ON_3$. Calculated %: C 59.65; H 8.34.

The aldehyde was oxidized with moist silver oxide to the corresponding acid. To do this, a solution of 25 g of the aldehyde in 500 ml of ethyl alcohol was mixed with a solution of 65 g of silver nitrate in 350 ml of water in a 2 liter flask, which was shaken continuously by machine for 4 hours; during this process, a solution

of 30 g of caustic soda in 1.2 liters of water was dropped in. After addition of the caustic soda solution, the shaking was continued for another 8 hours. After removal of the precipitate of silver, the filtrate was evaporated in vacuum to a small volume, acidified with dilute sulfuric acid (1:5), and the acid which separated was carefully extracted with ether. After the ether was driven off, there remained a thick oil; this was distilled at 138-139° at 20 mm. It then quickly crystallized. There was obtained 25 g (89% based on the aldehyde) of 2-methyl-Δ^3-cyclohexene carboxylic acid with m.p. 52-52.5° (from petroleum ether), in the form of transparent yellowish needles. The silver salt was obtained.

0.3826 g substance: 0.1669 g Ag.
Found %: Ag 43.63.
$C_8H_{11}O_2Ag$. Calculated %: Ag 43.67.

By means of the acid chloride (from 7 g of acid and 10.5 g of finely pulverized phosphorus pentachloride) there was obtained the amide of the crystalline form of 2-methyl-Δ^3-cyclohexenecarboxylic acid with m.p. 157-158° (from water). (It was impossible to obtain an amide from the liquid form).

0.1203 g substance: 0.3041 g CO_2; 0.1029 g H_2O.
Found %: C 68.94; H 9.57.
$C_8H_{13}ON$. Calculated %: C 69.03; H 9.41.

Ozonolysis, carried out according to the method described for the liquid form of 2-methyl-Δ^3-cyclohexene carboxylic acid, gave pentanetricarboxylic acid-1,3,4 with m.p. 177°; this gave no depression in a mixed test with the specimen obtained earlier.

3. The Condensation of Piperylene and Ethylidenemalonic Ester

25 g of ethylidenemalonic ester, synthesized by the method of Kommenos [14], 18 g of piperylene fraction, and 0.2 g of hydroquinone were heated in sealed tubes at 170-175° for 13 hours. After three fractional distillations, there was obtained 25.2 g (74% based on the ethylidenemalonate) of the diethyl ester of 2,6-dimethylΔ^3-cyclohexene-1,1-dicarboxylic acid. It was a transparent, thick liquid with a fresh, pleasant odor. B.p. 123-124° at 5 mm, 136-138° at 11 mm; n_D^{20} 1.4619; d_4^{20} 1.0416. MR_D 67.07. $C_{14}H_{22}O_4$ =. Calculated MR_D 67.49.

0.3259 g substance: 0.7840 g CO_2; 0.2525 g H_2O.
Found %: C 65.71; H 8.67.
$C_{14}H_{22}O_4$. Calculated %: C 66.11; H 8.71.

a) Saponification of the adduct. A solution of 15 g of the adduct in 45 ml of a 25% alcoholic solution of caustic potash was heated on the water bath at 90° for 8 hours. After cooling, the solution was diluted with water, and acidified with dilute hydrochloric acid (1:1). The crystalline precipitate which separated out was filtered off, and the filtrate evaporated to dryness in vacuum. The residue was extracted with dry ether, and the ether removed by heating; the crystalline residue was then united with the acid separated earlier, and recrystallized from ethylacetate (acrylonitrile was a good solvent for the recrystallization); it was obtained in the form of prisms with m.p. 188° (with decomp.). The yield of 2,6-dimethyl-Δ^3-cyclohexene-1,1-dicarboxylic acid obtained was 4.5 g (42%).

0.0972 g substance: 0.2145 g CO_2; 0.0613 g H_2O.
Found %: C 60.19; H 7.06.
$C_{10}H_{14}O_4$. Calculated %: C 60.59; H 7.12.

b) 4 g of the dicarboxylic acid was heated on an oil bath at 200° until no more CO_2 was given off. There was obtained 2,6-dimethyl-Δ^3-cyclohexene carboxylic acid. Upon recrystallization from ethyl acetate, it had the form of transparent yellowish needles with m.p. 55-56°. Yield 2.0 g (70%).

0.1213 g substance: 0.3107 g CO_2; 0.0987 g H_2O.
Found %: C 69.86; H 9.11.
$C_9H_{14}O_2$. Calculated %: C 70.10; H 9.15.

c) 1.5 g of the monocarboxylic acid and 3 g of selenium were heated in a sealed tube at 360° for 24 hours. The contents of the tube were fractionated to give a liquid which had a boiling point close to that of m-xylene (132-138° at 760 mm). This was oxidized by means of an alkaline 3% solution of potassium permanganate with boiling and continuous stirring. The manganese dioxide was filtered off, and the filtrate concentrated to a small volume and acidified with dilute hydrochloric acid (1:1). The white precipitate which formed was dried and had m.p. 341-343° (in a sealed capillary; copper block).

A mixed test with isophthalic acid showed no depression.

4. The Condensation of Piperylene with Benzalmalonic Ester

25 g of benzalmalonic ester, obtained by Allen's method [15], 14 g of piperylene, and 0.2 g of hydroquinone were heated in sealed tubes at 190° for 12 hours. After several fractional distillations, it was possible to separate from the mixture of unreacted benzalmalonic ester, dimer of piperylene, and tar, 12.5 g (39.3% based on the benzalmalonate) of the diethyl ester of 2-methyl-6-phenyl-Δ^3-cyclohexene-1,1-dicarboxylic acid. This was a colorless oil which refracted light very strongly, and had an indeterminate weak odor:

B.p. 170-172° at 4 mm; n_D^{20} 1.5206; d_4^{20} 1.1006; MR_D 87.40.
$C_{19}H_{24}O_4$ F 4. Calculated MR_D 86.99.

0.3290 g substance: 0.8661 g CO_2; 0.2271 g H_2O.
Found %: C 71.80; H 7.72.
$C_{19}H_{24}O_4$. Calculated %: C 72.12; H 7.65.

a) Saponification of the adduct. A solution of 8 g of the adduct in 25 ml of a 25% alcoholic solution of caustic potash was heated on the water bath at 90° for 12 hours. Upon cooling, the solution was diluted with water, acidified with dulute hydrochloric acid (1:1) and carefully extracted with ether. After removal of the ether by distillation, the residue began to crystallize. The acid, squeezed out on a porous plate and recrystallized from ethyl acetate (or from hot acrylonitrile), began to melt at 183° with the evolution of CO_2. It consisted of colorless needles, difficultly soluble in hot water, easily soluble in methanol and ethanol. Yield of 2-methyl-6-phenyl-Δ^3-cylcohexene-1,1-dicarboxylic acid, 3.5 g (54%).

0.1116 g substance: 0.2817 g CO_2; 0.0618 g H_2O.
Found %: C 68.84; H 6.19.
$C_{15}H_{16}O_4$. Calculated %: C 69.21; H 6.19.

b) 1 g of the dicarboxylic acid was heated on the oil bath at 190° until no more CO_2 was given off. The residue was in the form of a viscous syrup; it could not be made to crystallize. A silver salt was obtained.

0.0841 g substance: 0.0281 g Ag.
Found %: Ag 33.41.
$C_{14}H_{15}O_2Ag$. Calculated %: Ag 33.38.

c) 2 g of the dicarboxylic acid was dehydrogenated with 4 g of selenium in a sealed tube at 360° for 24 hours. A fairly viscous liquid was obtained, with an aromatic odor; this was oxidized by heating with a 3% alkaline solution of potassium permanganate, with continuous stirring. After filtration of the manganese dioxide the filtrate was concentrated to a small volume and acidified with dilute hydrochloric acid (1:1). The precipitate which formed was recrystallized from dilute alcohol; it melted at 159-161°. M.p. of 3-phenylbenzoic acid is given as 162° [11].

5. The Condensation of Piperylene and Ethylideneacetoacetic Ester

16 g of ethylideneacetoacetic ester obtained by Claisen's [18] method, 14 g of piperylene, and 0.2 g of hydroquinone were heated at 180° for 18 hours in sealed tubes. After separating the unreacted components, the piperylene dimer, and the tar, several fractional distillations gave 17 g (74% on the basis of the ethylideneacetoacetic ester) of the ethyl ester of 2,6-dimethyl-1-acetyl-Δ^3-cyclohexenecarboxylic acid. This was a colorless, oily liquid with a turpentine odor.

B.p. 116-118° at 5 mm; n_D^{20} 1.4724; d_4^{20} 1.0326; MR_D 60.97.
$C_{13}H_{20}O_3$ F. Calculated MR_D: 61.23.

0.1173 g substance: 0.2993 g CO_2; 0.0942 g H_2O.
Found %: C 69.59; H 8.98.
$C_{13}H_{20}O_3$. Calculated %: C 69.61; H 8.99.

7 g of the adduct was saponified with 10 ml of a 25% alcohol solution of caustic potash, by heating on a water bath at 90° for 6 hours. After cooling, the solution was diluted with water, and the oil which floated on top was extracted with ether. After removal of the ether by distillation, 2.1 g (45%) of 2,6-dimethyl-1-acetyl-Δ^3-cyclohexene was obtained. It was a colorless, fluid liquid with a mint odor.

B.p. 80-81° at 12 mm; n_D^{20} 1.4635; d_4^{20} 0.9259; MR_D 45.33.
$C_{10}H_{16}O$ F. Calculated MR_D 45.72.

0.0914 g substance: 0.2637 g CO_2; 0.0875 g H_2O.
Found %: C 78.69; H 10.71
$C_{10}H_{16}O$. Calculated %: C 78.89; H 10.59.

The semicarbazone was obtained by Zelinsky's method in the form of small white needles from dilute alcohol; m.p. 124°.

0.1499 g substance: 0.3477 g CO_2; 0.1232 g H_2O.
Found %: C 63.26; H 9.19.
$C_{11}H_{19}ON_3$. Calculated %: C 63.12; H 9.15.

After separation of the ketone, the aqueous layer was acidified with dilute sulfuric acid. It was noted that a great deal of CO_2 was evolved. The viscous oil which separated out soon began to crystallize. After removal to a porous plate and recrystallization from dilute alcohol, the acid, in the form of small needles, had m.p. 56° and appeared to be identical with the 2,6-dimethyl-Δ^3-cyclohexene-1-carboxylic acid obtained earlier, for a mixed test gave no depression. The silver salt was obtained.

0.0704 g substance: 0.0291 g Ag.
Found %: Ag 41.34.
$C_9H_{13}O_2Ag$. Calculated %: Ag 41.32.

6. The Condensation of Piperylene with Benzalacetoacetic Ester

16 g of benzalacetoacetic ester obtained by Flurscheim's method [17], 10 g of piperylene, and 0.1 g of hydroquinone were heated in a sealed tube at 180° for 20 hours. After separation of unreacted starting materials, piperylene dimer, and tar, by fractional distillation, two fractions were obtained:

1st: B.p. 165-167° at 4 mm; n_D^{20} 1.5288; d_4^{20} 1.0980 – to the amount of 9.3 g (44.5% on the basis of benzalacetoacetic ester);

2nd: B.p. 167-171° at 4 mm; n_D^{20} 1.5300 – 5.0 g.

The first fraction appeared to be the ethyl ester of 2-methyl-6-phenyl-1-acetyl-Δ^3-cyclohexene-1-carboxylic acid. It was a viscous, colorless syrup with

a turpentine odor:

MR_D 80.41. $C_{18}H_{22}O_3$ F_4. Calculated MR_D: 80.72.

0.1105 g substance: 0.3046 g CO_2; 0.0775 g H_2O.
Found %: C 75.18; H 7.85.
$C_{18}H_{22}O_3$. Calculated %: C 75.49; H 7.74.

The second fraction began to crystallize after a month. After being squeezed on a porous plate and recrystallized from methyl alcohol, it was in the form of transparent prisms with m.p. 61°. Yield 4.3 g (20.5% on the basis of benzalaceto-acetic ester).

0.1415 g substance: 0.3902 g CO_2; 0.0988 g H_2O.
Found %: C 75.21; H 7.81.
$C_{18}H_{22}O_3$. Calculated %: C 75.49; H 7.74.

Further investigation showed that the cyrstalline product was the ethyl ester of 3-methyl-2-phenyl-1-acetyl-Δ^4-cyclohexenecarboxylic acid.

a) Saponification of the adduct (1st fraction). A solution of 7 g of the adduct was saponified with 10 ml of a 25% alcoholic solution of caustic potash on the boiling water bath for 6 hours. The solution was diluted with water and the oil which separated out was extracted with ether. After removal of the ether by distillation, there was obtained 1.4 g (27%) of 2-methyl-6-phenyl-1-acetyl-Δ^3--cyclohexene with b.p. 150-156° at 10 mm, n_D^{20} 1.5301, in the form of a viscous liquid with a camphor odor.

0.1013 g substance: 0.3112 g CO_2; 0.0791 g H_2O.
Found %: C 83.78; H 8.74.
$C_{15}H_{18}O$. Calculated %: C 84.06; H 8.47.

After extraction of the ketone, the aqueous layer was acidified with dilute sulfuric acid (1:5). The 2-methyl-6-phenyl-Δ^3-cyclohexene-1-carboxylic acid separated out in the form of a viscous syrup which did not crystallize upon cooling to -15°, and distilled at 160-170° (5 mm). Yield 2.8 g (53%). The silver salt was obtained:

0.1053 g substance: 0.0353 g Ag.
Found %: Ag 33.52.
$C_{14}H_{15}O_2Ag$. Calculated %: Ag 33.38.

b) 2 g of the acid was dehydrogenated with 4 g of selenium in a sealed tube at 360° for 20 hours. The contents were extracted with ether. After removal of the ether by distillation, there remained a viscous liquid; this was oxidized by heating with a 3% alkaline solution of potassium permanganate, with continuous stirring. The manganese dioxide was filtered off, and the filtrate concentrated to a small volume, and acidified with dilute hydrochloric acid (1:1). The white precipitate which formed was recrystallized from dilute alcohol; it had m.p. 158-160° and appeared to be identical with the 3-phenylbenzoic acid obtained earlier.

c) Saponification of the adduct (2nd fraction) A solution of 4 g of the adduct in 10 ml of a 25% alcohol solution of caustic potash was heated on the boiling water bath for 4 hours. The solution was then diluted with water and extracted with ether. After removal of the ether by distillation, there was obtained 0.8 g (26%) of 3-methyl-2-phenyl-1-acetyl-Δ^4-cyclohexene, in the form of an oily liquid with a turpentine odor. The semicarbazone, obtained by Zelinsky's method, had m.p. 195° (from methyl alcohol).

0.1196 g substance: 0.3104 g CO_2; 0.0860 g H_2O.
Found %: C 70.78; H 8.04.
$C_{16}H_{21}ON_3$. Calculated %: C 70.82; H 7.81.

After extraction of the ketone, the aqueous layer was acidified with dilute hydrochloric acid (1:1). The viscous oil which separated out began to crystallize after a day; the crystals were squeezed out on a porous plate and recrystallized from aqueous methyl alcohol. There was thus obtained 2.1 g (70%) of 3-methyl-2-phenyl-Δ^4-cyclohexene-1-carboxylic acid with m.p. 83°.

0.1104 g substance: 0.3137 g CO_2; 0.0747 g H_2O.
Found %: C 77.49; H 7.57.
$C_{14}H_{16}O_2$: Calculated %: C 77.74; H 7.46.

c) 1.8 g of the acid was dehydrogenated with 3 g of selenium in a sealed tube at 360° for 20 hours. The contents of the tube were extracted with ether; after removal of the ether by distillation, a yellowish oil was obtained; this was oxidized by heating and shaking continuously with a 3% alkaline solution of potassium permanganate. The manganese dioxide was filtered off and the filtrate concentrated to a small volume and acidified with dilute hydrochloric acid (1:1). The precipitate which settled out was recrystallized from dilute alcohol; it had m.p. 112-113°. The literature gives for 2-phenylbenzoic acid, m.p. 113.5-114.5°.

SUMMARY

1. Addition products of piperylene with acrylonitrile, acrolein, ethylidenemalonic and ethylideneacetoacetic esters, benzylidenemalonic and benzylideneacetoacetic esters, have been obtained by the diene synthesis.

2. The structure of these addition products has been determined.

3. It has been shown that the manner of addition to piperylene of the dienes mentioned is in good accord with the directions of polarization of the piperylene and the dieneophile.

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INVESTIGATIONS ON THE TRANSFORMATION OF PINACONES WITH SUBSTITUENT ACETYLENE RADICALS

VII. SYNTHESIS AND TRANSFORMATION OF METHYL-DIPHENYL-TERTIARYBUTYLACETYLENYL ETHYLENE GLYCOL

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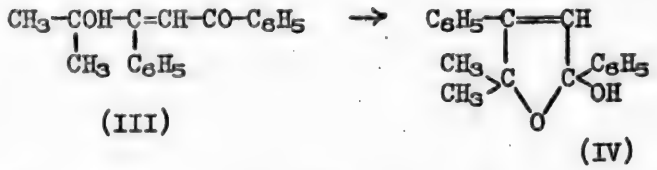
During an investigation of the isomerization of dimethyl-phenyl-phenylacetylenyl ethylene glycol (I) (2-methyl-3,5-diphenylpentine-4-diol-2,3) into 5,5-dimethyl-2,4-diphenyl-2-hydroxy-dihydrofuran-2,5 (IV), we suggested [1] that this transformation proceeds in the manner of the acetylene-allene rearrangement, with the formation at first of an unstable hydroxyallene (II), which is then transformed into an unsaturated γ-ketoalcohol (III), and finally forms a ring to give the substituted hydroxy-dihydrofuran (IV):

(I) (II)



(III) (IV)

The γ-ketoalcohol (III) from the dimethyl-phenyl-phenylacetylenyl ethylene glycol (I) could not be detected, and the single product of the reaction was the substituted hydroxydihydrofuran (IV).

Similar results were also obtained with dimethyl-p-tolyl-phenylacetylenyl ethylene glycol [2].

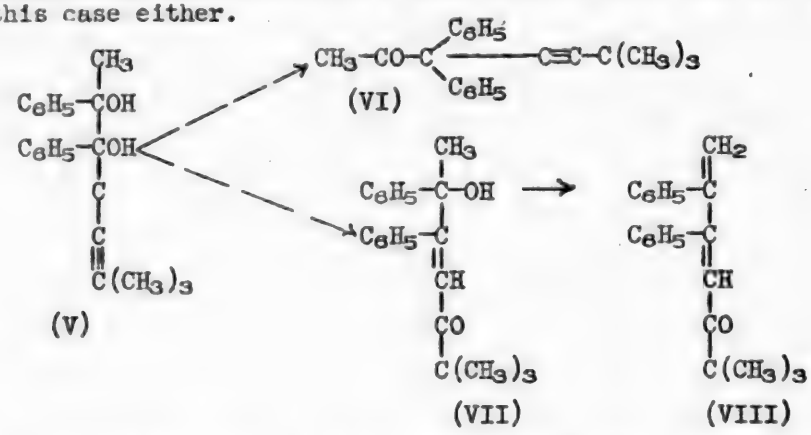
However, by substituting the tertiarybutylacetylenyl radical for the phenylacetylenyl radical, i.e., by using dimethyl-phenyl-tertiary butylacetylenyl ethylene glycol (2,6,6-trimethyl-3-phenyl-heptine-4-diol-2,3), the corresponding γ-ketoalcohol was obtained along with the substituted hydroxy dihydrofuran; their reciprocal transitions were determined under the catalytic action of sulfuric acid [3].

As a result of the isomerization of methyl-diphenyl-phenylacetylenyl ethylene glycol (2,3,5-triphenyl-pentine-4-diol-2,3) there was also found an unsaturated γ-ketoalcohol; it was not possible, however, to obtain this in pure form, as vacuum distillation caused its cleavage into acetophenone and benzalacetophenone.

Considering that the tertiarybutylacetylenyl residue of dimethyl-phenyl-tertiary-butylacetylenyl ethylene glycol stabilized the corresponding γ-ketoalcohol [3], we decided to obtain the unsaturated γ-ketoalcohol by isomerization of methyl diphenyl-tertiarybutylacetylenyl ethylene glycol (2,3-diphenyl-6,6-dimethylheptine-4-diol-2,3) in order to make a more thorough investigation of this interesting and little studied class of unsaturated hydroxyketones.

In order to obtain the unsaturated γ-ketoalcohol, we synthesized methyl-diphenyl-tertiarybutylacetylenyl ethylene glycol (V) and treated it under the usual conditions with sulfuric acid; we thus isolated a liquid substance which upon distillation in vacuum, in contradistinction to the γ-ketoalcohol which had been studied earlier [4], 2,3,5-triphenyl-pentene-3-ol-2-one-5, did not undergo ketone cleavage, but gave up water and was transformed into the diene ketone – 2,3-diphenyl-6,6-dimethyl-heptadiene-1,3-one-5 (VIII).

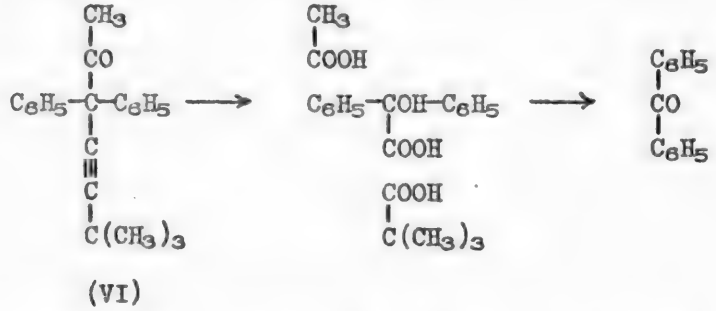
Consequently, the individual γ-ketoalcohol (VII) was not successfully isolated in this case either.



The original pinacone, 2,3-diphenyl-6,6-dimethyl-heptine-4-diol-2,3 (V) was synthesized in the usual way and was characterized by greater stability than was ascribed in a preceding communication to 2,3,5-triphenyl-pentine-4-diol-2,5 (sym.-methyl-diphenylphenylacetylenyl ethylene glycol) [4], as upon heating in vacuum cleavage took place to only a small degree, and the main portion of the product distilled without decomposition. In this case, the great volatility of the pinacone was ascribable to the tertiarybutylacetylenyl residue.

The pinacone which had been synthesized underwent the pinacoline and acetylene-allene transformations under the action of both 20 and 30% sulfuric acid.

As a result of the pinacoline rearrangement, a ketone of the acetylene series, 3,3-diphenyl-6,6-dimethyl-heptine-4-one-2 (VI) was obtained; its structure was established by its oxidation to give a mixture of acetic, benzilic, and trimethylacetic acids, and benzophenone, which was a product of the further oxidation of benzilic acid:



Consequently, in this case, as in the cases of all the pinacones previously investigated by us, the greatest mobility was possessed by the hydroxyl group attached to the carbon atom which was bound to the acetylene residue of the pinacone.

At a higher concentration of acid, the yield of ketone was increased; thus,

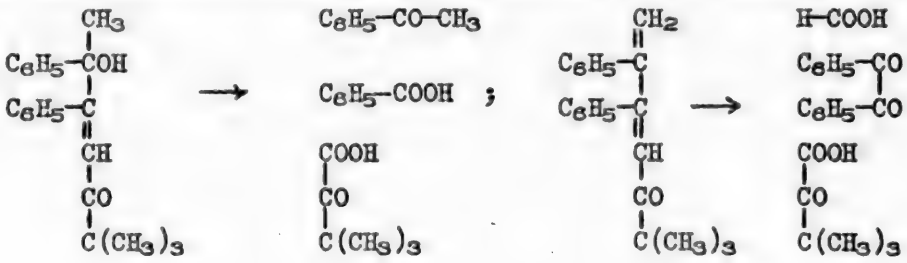
with 20% sulfuric acid, the yield amounted to 10.9%, and with 30%, rose to 44.8% of theory.

The acetylene-allene rearrangement took place alongside the pinacoline, and led to an unstable, unsaturated γ-ketoalcohol, 2,3-diphenyl-6,6-dimethyl-heptene-3-ol-2-one-5 (VII).

In this case, we find completely applicable the scheme of rearrangement suggested for methyl-diphenyl-phenylacetylenyl ethylene glycol in a preceding communication [4]; this takes place through the medium of an organic cation, whose two mesomeric forms give from the beginning two reactions, which take place parallel to each other.

As has already been noted, the unsaturated γ-ketoalcohol (VII) has been shown to be unstable, despite the fact that upon distillation under reduced pressure it did not split into acetophenone and an unsaturated ketone, like the 2,3,5-triphenyl-pentene-3-ol-2-one-5 [4] investigated earlier, but gradually gave off water in vacuum, to form a diene ketone, 2,3-diphenyl-6,6-dimethyl-heptadiene-1,3-one-5 (VIII). This diene ketone was isolated in pure form by the action of acetic anhydride upon the mixture of unsaturated γ-ketoalcohol and diene ketone, and was characterized in the form of its semicarbazone.

The oxidation of the mixture of these two substances gave acetophenone, benzoic, and trimethylpyruvic acid, showing the presence of the unsaturated γ-ketoalcohol (VII), and in addition it gave benzil and formic acid, which because of the presence of the trimethylpyruvic acid corresponded to the diene ketone (VIII):



(VII) (VIII)

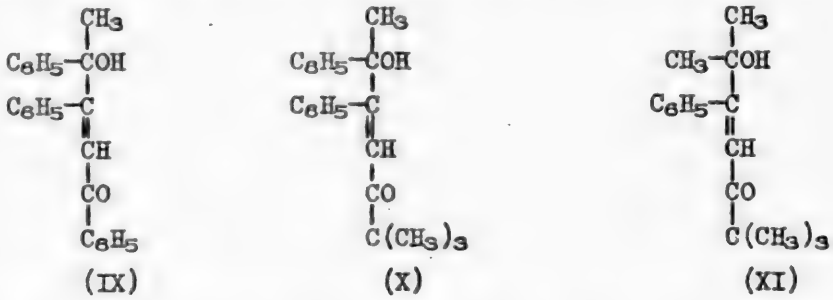
The literature gives the tendency of different alcohols to undergo dehydration. Dehydration takes place with especial ease with α-ethylene alcohols, which split off water even upon distillation in vacuum [5].

The difference in the behavior upon heating of the two γ-ketoalcohols investigated — the ketone cleavage of 2,3,5-triphenyl-pentene-3-ol-2-one-5 [4] and the dehydration of 2,3-diphenyl-6,6-dimethyl-heptene-3-ol-2-one-5 — is not due to their structure (the C_6H_5 and $C(CH_3)_3$ residues) but can be explained by means of the conditions of experiment, as according to the data of Grignard and Chambret [5], one and the same alcohol may be changed in either direction, depending upon the degree of heating. At a lower temperature dehydration takes place, at a higher the ketone cleavage occurs.

We must note that among the products of the transformation of methyl-diphenyl-tertiarybutylacetylenyl ethylene glycol, almost no substituted hydroxydihydrofuran was observed as a product of ring-formation by the unsubstituted γ-ketoalcohol; similarly, under the action of 30% sulfuric acid, despite the fact that fluorescence of the acid solution was observed as a result of the formation of an oxonium salt, upon neutralization of the solution, only negligible traces of the compound could be separated; in the case of the 20% acid, the fluorescence was in general very weak.

Of all the pinacones we investigated, methyl-diphenyl-tertiarybutylacetylenyl ethylene glycol (V) gave the smallest yield of substituted hydroxydihydrofuran under the action of sulfuric acid (inner partial ketal), while dimethyl-phenyl-phenylacetylenyl ethylene glycol (I) [8] was completely transformed into a substituted hydroxydihydrofuran (IV). As has been noted above, the transformation from a pinacone to a substituted hydroxydihydrofuran takes place by way of the unsaturated γ-ketoalcohol, whose tendency to ring-formation, in the manner of formation of an acetal, determines the yield of hydroxydihydrofuran.

Upon comparing the structure of the three intermediate γ-ketoalcohols (IX,X,XI):



(IX) (X) (XI)

it was found that upon substitution of the phenyl which was next to the carbonyl group by tertiary butyl, the tendency to ring-formation was diminished (IX and X), just as it was diminished by substituting one of the methyl groups on the alcohol carbon by phenyl (X and XI).

This observation of ours is in agreement with the results of the work of Adkins [7], who investigated the equlibrium mixtures of aldehydes and alcohols with their acetals. He found that the substitution of phenyl in the aldehyde by an aliphatic radical with a branched carbon chain led to the lowering of the acetal content in the equilibrium mixture, just as did the substitution of the aliphatic residue on the alcohol carbon by phenyl.

EXPERIMENTAL

1. Synthesis of Methyl-diphenyl-tertiarybutylacetylenyl Ethylene Glycol

As starting materials to obtain this glycol, we used methylbenzoin and tertiary butylacetylene.

Methylbenzoin was obtained from benzil and methylmagnesium iodide [8] in a yield of 55.7% of theory; m.p. 65-66° [9]. Tertiarybutylacetylene was synthesized from pinacone hydrate, by way of pinacoline and the corresponding chloride [10]. Yield 30%, calculated on the basis of pinacoline; b.p. 37-38°.

To tertiarybutylacetylenyl magnesium bromide, prepared in the usual way, an ether solution of methyl benzoin was added drop by drop, with vigorous stirring. The mixture was allowed to react for three days, being stirred continuously for 2 days at ordinary temperature, and heated for 1 day with gentle boiling of the ether. After decomposition with water and dilute acid, the compound was extracted with ether, and the ether extract was washed with a solution of soda in water and dried over sodium sulfate. After the ether had been removed by distillation, there remained a viscous, transparent liquid with a bright yellow color.

Four experiments for the synthesis of the pinacone were carried out. From 22 g of magnesium, 74 g of tertiarybutyl acetylene, and 85.1 g of methylbenzoin, 105 g of crude pinacone were obtained.

The thick, very viscous substance obtained was distilled in vacuum at 2 mm.

pressure; it boiled at 160-163° (most of it at 161°). During distillation, the formation of a small low-boiling fraction was observed; this contained acetophenone, characterized by means of its semicarbazone. Upon standing for a year and a half, the chief fraction began to crystallize; the melting point of the crystals was 53-55°. The yield of pure product was 68 g., or 59% of theory, calculated on the basis of the original methylbenzoin.

Analysis of pinacone with b.p. 160-163° at 2 mm:

0.1259 g substance: 0.3775 g CO_2; 0.0872 g H_2O.
0.1253 g substance: 0.3750 g CO_2; 0.0891 g H_2O.
Found %: C 81.77, 81.69; H 7.70, 7.90.
$C_{21}H_{24}O_2$. Calculated %: C 81.81; H 7.79.

Determination of molecular weight:

0.5085 g substance: 19.18 g C_6H_6: Δt 0.45°.
Found: M 294.6
$C_{21}H_{24}O_2$. Calculated: M 308.

Determination of number of hydroxyl groups, according to Terentyev.

0.0676 g substance: 10.8 ml CH_4 (13°, 759 mm).
Found: v_o 9.95 ml; % OH 11.16.
$C_{21}H_{22}(OH)_2$. Calculated: v_o 9.83 ml; % OH 11.03.

Upon heating the pinacone with freshly calcined potash [11], an acetylene hydrocarbon was observed, causing turbidity in an ammoniacal solution of silver oxide.

2. Action of Sulfuric Acid on Methyl-diphenyl-tertiarybutylacetylenyl Ethylene Glycol

Experiment 1. A mixture of 30 g of pinacone and a 10-fold amount of 30% sulfuric acid was heated to boiling with vigorous stirring for 3 hours. The aqueous solution was weakly fluorescent, and an oily layer separated out on the surface. Two ether extracts were made of the cooled solution: one of the acid solution one after neutralization with a soda solution. Both ether extracts were dried over sodium sulfate.

After removal of the ether from the extract of the acid solution by distillation, there was obtained a thick dark yellow oil (27 g), in which crystals soon began to form. After separation from the oil and washing on a porous plate with petroleum ether, the crystals were recrystallized from hot petroleum ether; they melted at 79-80°. By this method, 11.2 g (44.8%, assuming the substance to be the ketone) of a white finely crystalline substance was obtained. This gave no reaction for hydroxyl groups, and did not decolorize a cold solution of potassium permanganate. The oily substance which remained after separation of the crystals gave off a copious quantity of blistering gas under the action of methyl magnesium iodide, quickly decolorized a solution of potassium permanganate, and reacted with a solution of bromine in chloroform. The yield of liquid material was 15 g (or 50% if we assume it to be unsaturated γ-ketoalcohol).

Upon removal by distillation of the ether from the extract of the neutral solution, a small amount of material was obtained, insufficient for investigation.

Experiment 2. 11.7 g of the glycol was treated with 20% sulfuric acid under the same conditions as in the preceding experiment. There was hardly any fluorescence; 10.6 g of an oily liquid was separated from the acid ether extract. After several days, about 1.2 g of crystalline substance separated out of this, with m.p. 79-80°. Yield 10.9%, assuming the material to be ketone.

The liquid remaining after separation of the crystalline product was observed

to have the same properties as the liquid obtained in the 1st experiment. The ether extract from the neutralized solution did not contain any product.

3. The Acetylenyl Ketone, 3,3-Diphenyl-6,6-dimethyl-heptine-4-one-2 (VI)

The substance with m.p. 79-80° was very soluble in ether, benzene, alcohol, acetone, and pyridine, and slightly soluble in petroleum ether. It formed a semicarbozone with m.p. 202-203°.

Analysis of the compound with m.p. 79-80°:

0.1224 g substance: 0.3890 g CO_2; 0.0854 g H_2O.
0.1149 g substance: 0.3650 g CO_2; 0.0793 g H_2O.
Found %: C 86.67, 86.63; H 7.75, 7.66.
$C_{21}H_{22}O$. Calculated %: C 86.89; H 7.58.

Determination of the molecular weight:

0.4624 g substance: 17.26 g C_6H_6: Δt 6.5°.
Found: M 268.
$C_{21}H_{22}O$. Calculated: M 290.

Analysis of the semicarbazone with m.p. 202-203°:

0.1494 g substance: 0.4165 g CO_2; 0.0962 g H_2O.
0.1399 g substance: 14.9 ml N_2 (22°, 759.5 mm).
0.1233 g substance: 13.1 ml N_2 (22°, 750.5 mm).
Found %: C 76.03; H 7.15; N 12.31, 12.14.
$C_{22}H_{25}ON_3$. Calculated %: C 76.08; H 7.20; N 12.10.

According to these data, the substance with m.p. 79-80° was the ketone.

To determine the structure of this substance, it was oxidized with a solution of potassium permanganate.

Oxidation of the substance with m.p. 79-80°. The oxidation was carried out in a water-pyridine solution. For purposes of oxidation, 4 g of the substance was taken, and 5.8 g of potassium permanganate (based on the calculation of 8 molecules of $KMnO_4$ to 3 molecules of ketone).

To the solution of 4 g of ketone in 95 ml of pyridine was added a solution of 3 g of potassium permanganate in 110 ml of water, preheated to 40°. After 5 hours of vigorous stirring, the remaining 2.8 g of potassium permanganate, in the form of small portions of a fine powder, was sprinkled into the dark brown solution. Stirring was continued for 13 hours in all, the last 3 hours with heating to 40-50°.

After the end of the oxidation, the manganese dioxide was filtered off from the liquid, washed twice with small amounts of water, and extracted several times with ether. The ether extract contained the original ketone to the amount of 1.3 g, with m.p. 78-80° (it gave no depression of the melting point in a mixed test with the original substance).

From the filtrate, to which the wash water had been added, the excess of solvent, together with neutral products of oxidation, were distilled off by heating gently on the boiling water bath. The pyridine of the distillate was combined with the calculated quantity of sulfuric acid, and that part of the neutral product of reaction which was volatile with steam, extracted with ether. After removal of the ether by distillation, 0.2 g of a quickly solidifying oil was obtained. The melting point of the crystalline substance, which appeared to be benzophenone, was 47-48°; mixed with a known sample of benzophenone, it gave no lowering of the melting point. A semicarbazone was obtained with m.p. 165-166°, corresponding to the semicarbazone of benzophenone.

The neutral product of oxidation, not volatile with steam, was extracted with ether. After removal of the ether, there was obtained an oil (0.6 g), part of which began to crystallize. The crystalline mass was washed with alcohol on a porous filter plate. The purified substance (0.25 g) was the original ketone (mixed test), and the product soluble in alcohol was benzophenone (mixed test).

To separate the acid products of oxidation, the solution containing the salts of organic acids which remained after separation of the neutral products was concentrated on the water bath and decomposed with dilute sulfuric acid. The volatile acids were driven off by heating and collected in two fractions, which were transformed into the silver salts by boiling with freshly prepared silver carbonate. By partial recrystallization, the salt was separated into several fractions, in which the percentage of silver was determined.

Analysis of the salts from distillate I:

1st fraction: 0.0956 g salt: 0.0498 g Ag; % Ag 52.09.
3rd fraction: 0.1331 g salt: 0.0735 g Ag: % Ag 55.13.
4th fraction: 0.1215 g salt: 0.0753 g Ag; % Ag 61.14.

Analysis of the salts from distillate II:

1st fraction: 0.0817 g salt: 0.0423 g Ag; % Ag 51.77.
3rd fraction: 0.1113 g salt: 0.0649 g Ag; % Ag 58.31.
5th fraction: 0.1212 g salt: 0.0781 g Ag; % Ag 64.44.
$(CH_3)_3$ COOAg. Calculated %: Ag 51.67.
CH_3COOAg. Calculated %: Ag 64.65.

Therefore, the first distillate fractions (mostly the first) contained the trimethylacetic acid, and the later ones, acetic acid.

The acids which were not volatile with steam were extracted with ether after the removal of the volatile acids. The residue after distillation of the ether gave a clear red color with sulfuric acid; this is characteristic of benzilic acid. The residue was dissolved in absolute ether and saturated with dry ammonia. The ammonium salt was transformed into the silver salt, which was analyzed.

0.0994 g substance: 0.1830 g CO_2; 0.0318 g H_2O.
0.0902 g substance: 0.0298 g Ag.
Found %: C 50.21; H 3.49; Ag 32.39.
$C_{14}H_{11}O_3Ag$. Calculated %: C 50.01; H 3.28; Ag 32.24.

The data obtained correspond to benzilic acid.

Thus, on the basis of the products of oxidation – acetic, trimethylacetic, and benzilic acids, and benzophenone, we may ascribe to the ketone the structure corresponding to diphenyl-tertiarybutylacetylenyl-acetyl methane (3,3-diphenyl-6,6-dimethyl-heptine-4-one-2).

4. The Unsaturated γ-Ketoalcohol, 2.3-Diphenyl-6,6-dimethyl-heptene-3-ol-2-one-5 (VII)

The liquid oily substance that remained in experiments I and II after the separation of the crystalline ketone gave the reaction for the hydroxyl group, and had an unsaturated character.

Upon vacuum distillation at 3.5 mm, the liquid (obtained by the action of 30% sulfuric acid; experiment 1) gave three fractions; there was a great deal of tar in the residue. The middle, largest fraction, with b.p. 160-166° (3.5 mm) contained a substance which had a content of 84.73% in carbon, while the content for the unsaturated γ-ketoalcohol corresponded to 81.81% carbon, and for the product of the latter's dehydration, to 86.89%. A determination of thehydroxyl groups

by Terentyev's method gave 4.87% hydroxyl, whereas theory, calculated on the basis of one hydroxyl in the unsaturated γ-ketoalcohol, required 5.52%; the molecular weight, determined by the cryoscopic method, was 303.8.

The oily liquid (10.5 g) obtained by the action of 20% sulfuric acid on the pinacone (experiment II), was also subjected to distillation in vacuum at 2 mm. The first fraction, with b.p. 136-158°, upon analysis for carbon, also had a higher carbon content (84.17%) than the theory required.

This fraction was distilled several times in vacuum, and in every case, considerable frothing of the liquid was noticed; low-boiling fractions were obtained, with a wide boiling range, and a considerable quantity of tar-formation was accompanied by an increased percentage of carbon after each distillation.

The vacuum distillation was therefore unsuccessful in separating individual products, as in the process of distillation, the compound changed, apparently giving off water.

In order to determine the composition of this mixture, we subjected to oxidation the fraction that boiled at 140-150° at 2 mm pressure and had an average carbon content of 84 to 85%.

Oxidation of the liquid substance with b.p. 140-150° at 2 mm. We took 5.3 g of the substance and 10.4 g of potassium permanganate in the form of a 2% aqueous solution (this was 1.3 g in excess of the theoretical quantity calculated for the unsaturated ketoalcohol). The oxidation took place at room temperature upon energetic stirring for 12 hours, followed by 4 more hours at 40°. Complete decolorization was not attained. The solution was decolorized with sodium sulfite slightly alkalinized with soda, and filtered off from the manganese dioxide. The filtrate and the manganese dioxide were extracted with ether, and the latter distilled off; the yellow oily substance was fractionally distilled with steam. Ether extracts were made of the 7 fractions obtained. The residue which did not distill over with steam was also extracted with ether.

After removal of the ether by distillation, the 1st and 2nd fractions gave acetophenone, characterized by means of its semicarbazone, with b.p. 200-201°; this gave no lowering of the melting point in a mixture with a known sample of acetophenone semicarbazone. The smallest fractions – the 3rd and 4th – also gave a semicarbazone of acetophenone, but less pure. The total quantity of acetophenone amounted to 0.8 g.

After removal of the ether by distillation, the 5th, 6th, and 7th fractions gave a yellow oil, which solidified into a mass of yellow needles. The residue, which did not distill over with steam, after distillation of the ether, also solidified to give yellow needle-shaped crystals. After recrystallization from alcohol, the substance was obtained in the form of small yellow needles, which melted at 94-95°, gave no lowering of the m.p. with a known preparation of benzil, and showed the characteristic qualitative reaction for benzil – a purplish red color upon heating an alcoholic solution with concentrated alkali solution. The total amount of benzil isolated was 1 g.

The acid products of oxidation, separated in the usual manner by acidification with dilute sulfuric acid, contained benzoic acid, which was isolated in solid form as a light white mass. After sublimation it melted at 119-120°, and gave no lowering of the melting point with a known sample of benzoic acid. In addition to the benzoic acid, traces of formic acid were observed in the first distillate when the acid was removed by boiling. This distillate caused cloudiness in a saturated solution of mercuric chloride, gave a precipitate insoluble in alcohol with lead nitrate, and a blackening of the precipitate with an ammoniacal solution of silver oxide upon heating. The silver salt of the following

fractions darkened considerably when their solutions were concentrated, so that it was impossible to analyze them.

The acids which were non-volatile with steam were extracted with ether, and after the latter was removed, appeared as a thick liquid which solidified after standing in a dessicator for 2 months. The melting point of the crystals was 87.5-89°. According to the literature [12], trimethylpyruvic acid melts at 90-91°.

A part of the crystals were transformed by way of the ammonia salt into the silver salt, which was analyzed.

0.1304 g salt; 0.0592 g Ag
0.0804 g salt; 0.0368 g Ag.
Found %: Ag 45.39, 45.77.
$C_8H_9O_3Ag$. Calculated %: Ag 45.57.

Another part of the acid was treated in a solution of methyl alcohol with hydrazine hydrate; the evolution of heat was observed, and a yellow product separated, which after recrystallization from hot methyl alcohol melted at 203-204°. According to the literature [13], the azine of trimethylpyruvic acid melts at 207°.

Acetophenone and benzoic acid could be formed by the oxidation of an unsaturated γ-ketoalcohol and benzil and formic acid by the oxidation of a diene ketone; trimethylpyruvic acid could be obtained by oxidation of either substance.

The products of oxidation obtained give reason to conclude that the unsaturated γ-ketoalcohol is an unstable substance and that it gradually evolves water during vacuum distillation, forming a mixture of ketoalcohol and diene ketone.

5. The Diene Ketone, 2,3-Diphenyl-6,6-dimethyl-heptadiene-1,3-one-5 (VIII)

In view of the fact that the γ-ketoalcohol evolved water upon distillation in vacuum, and was transformed into a diene ketone, it was decided to dehydrate the ketoalcohol by means of acetic anhydride. For this purpose, 5 g of the liquid obtained by the action of sulfuric acid upon pinacone was mixed with an equal volume of acetic anhydride and heated on an oil bath to 155° for 1.5 hours. The excess of acetic anhydride was decomposed with water, and the heavy dark mass which separated on the bottom of the flask was extracted with ether. After removal of the ether by distillation, the residue was distilled in vacuum at 156-159° (3.5 mm). Yield, 2.4 g; there was considerable tar in the residue.

The light-yellow, fluid liquid obtained quickly decolorized an aqueous solution of potassium permanganate, gave off no gas under the action of methylmagnesium iodide, and gave a semicarbazone in the form of excellently shaped crystals with m.p. 204-205°. A mixed test with the semicarbazone of the acetylene ketone gave a lowering of the melting point.

Analysis of the substance with b.p. 156-159° at 3.5 mm:
0.1004 g substance: 0.3192 g CO_2; 0.0683 g H_2O.
Found %: C 86.71; H 7.56.
$C_{21}H_{22}O$. Calculated %: C 86.89; H 7.58.

Analysis of the semicarbazone with m.p. 204-205°.
0.1232 g substance: 13.1 ml N_2 (18°, 765 mm).
0.0961 g substance: 10.5 ml N_2 (19°, 748 mm).
Found %: N 12.30, 12.30.
$C_{22}H_{25}ON_3$. Calculated %: N 12.10.

According to the analytical data, the substance with b.p. 156-159° at 3.5 mm was the unsaturated ketone, 2,3-diphenyl-5,6-dimethyl-heptadiene-1,3-one 5.

In order to confirm the structure of the diene ketone, 1.2 g of the substance was oxidized with potassium permanganate (130 ml of 2% solution) at room temperature, with vigorous stirring. Browning of the solution took place very quickly, and the oxidation was completed in 4 hours; a deposit of crystalline material was formed on the walls of the flask. The manganese dioxide was filtered off, and the precipitate and filtrate then treated with ether. After removal of the ether, a yellow crystalline substance was obtained (0.6 g) with m.p. 93-94°; it gave no lowering of the melting point with a known sample of benzil.

Among the acid products which were volatile with steam, qualitative reactions conducted in the usual way showed the presence of traces of formic acid. The acid not volatile with steam melted at 85-86°; the silver salt was obtained by way of the ammonium salt. The silver salt was analyzed and corresponded to a salt of trimethylpyruvic acid.

0.1011 g salt: 0.0458 g Ag.
0.1223 g salt: 0.0558 g Ag.
Found %: Ag 45.53; 45.62.
$C_6H_9O_3Ag$. Calculated %: Ag 45.57.

The products of oxidation — benzil, formic, and trimethylpyruvic acids — confirmed the suggested structure for the diene ketone as being 2,3-diphenyl-6,6-dimethyl-heptadiene-1,3-one-5.

SUMMARY

1. Methyl-diphenyl-tertiarybutylacetylenyl ethylene glycol, or 2,3-diphenyl-6,6-dimethylheptine-4-diol-2,3 has been prepared for the first time, and its rearrangements under the action of sulfuric acid of different concentrations have been studied.

It has been found that an acetylene ketone, 3,3-diphenyl-6,6-dimethyl-heptine-4-one-2 is formed as a product of the pinacoline rearrangement, and a γ-ketoalcohol, 2,3-diphenyl-6,6-dimethyl-heptene-3-ol-2-one-5, as an unstable product of the acetylene-allene rearrangement.

2. It has been found that both upon distillation of the unsaturated γ-ketoalcohol, and upon its treatment with acetic anhydride, dehydration takes place, and a diene-ketone, 2,3-diphenyl-6,6-dimethyl-heptadiene-1,3-one-5 is formed. The γ-ketoalcohol, however, does not form a ring to give a substituted hydroxydihydrofuran, thus differing from the γ-ketoalcohols previously investigated.

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* See CB translation p. a197 ff.

THE ACETYLENE-ALLENE REARRANGEMENTS

1. THE ACTION OF PHOSPHOROUS ACID ESTERS ON 2-METHYL-2-CHLOROBUTINE-3

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In a preceding communication [1], devoted to a study of allyl rearrangemdnts, we investigated the action of salts of dialkylphosphorous acids and of phosphorous acid esters on isomeric methoxychloropentenes. It was shown that the reaction between the primary chloride, 1-methoxy-5-chloropentene-3, and the sodium salts of dialkylphosphorous acids took place normally, without an allyl rearrangement, to give the corresponding 1-methoxy-5-dialkylphosphone-3-pentenes. The reaction between the secondary chloride, 1-methoxy-3-chloropentene-4 and the sodium salts of dialkylphosphorous acids in the presence of free dialkylphosphorous acids in the reaction medium took place ionically, with a complete allyl rearrangement, and led to the formation of the same 1-methoxy-5-dialkylphosphone-3-pentenes.

$$CH_3OCH_2CH_2CHClCH{=}CH_2 \longrightarrow \left[\begin{array}{l} CH_3OCH_2CH_2 - \overset{+}{C}H - CH = CH_2 \\ CH_3OCH_2CH_2 - CH = CH - \overset{+}{C}H_2 \end{array}\right] + NaOP(OR)_2 \longrightarrow$$

$$\longrightarrow CH_3OCH_2CH_2CH = CH - CH_2 - P(=O)(OR)_2$$

In the absence of free dialkylphosphorous acids in the reaction medium, the corresponding methoxy-di-(dialkylphosphone)-pentanes were obtained; these were formed by the further reaction of the methoxyphosphonepentenes with the salt of the dialkylphosphorous acid.

The reaction between the primary chloride, 1-methoxy-5-chloropentene-3 and the esters of phosphorous acid takes place normally, without rearrangement, to give the corresponding methoxydialkylphosphonepentenes.

In the progress of this work, it seemed to us of interest to investigate the reactions of the esters of phosphorous acid and the salts of the dialkyl phosphorous acids with the acetylene chloride, 2-methyl-2-chlorobutine-3.

As was shown by the investigations of T.A.Favorskaya [2], this chloride as well as others structurally like it, in the presence of cuprous chloride and hydrochloric acid, isomerize to give allene chlorides, and then diene chlorides.

Saponification of the allene chloride results in rearrangement; a dimethylethinal carbinol is formed.

A.N.Zakharova investigated the reaction of acetylene chlorides with silver acetate [3], methylmagnesium iodide, and phenylmagnesium bromide [4]. The reaction between silver acetate and 2-chloro-2-methylbutine-3 leads to the formation of a mixture of isomeric acetates, and with 2-chloro-2-methylpentine-3 only to an acetate of the allene compound. The reaction between 2-chloro-2-methylpentine-3 and magnesium organic compounds also gives chiefly a hydrocarbon of the allene type.

With regard to the mechanism of this reaction, we must say that we have at present no definite picture of it, although it appears that it may possibly be analogous to the reactions taking place with allyl rearrangements, whose mechanisms

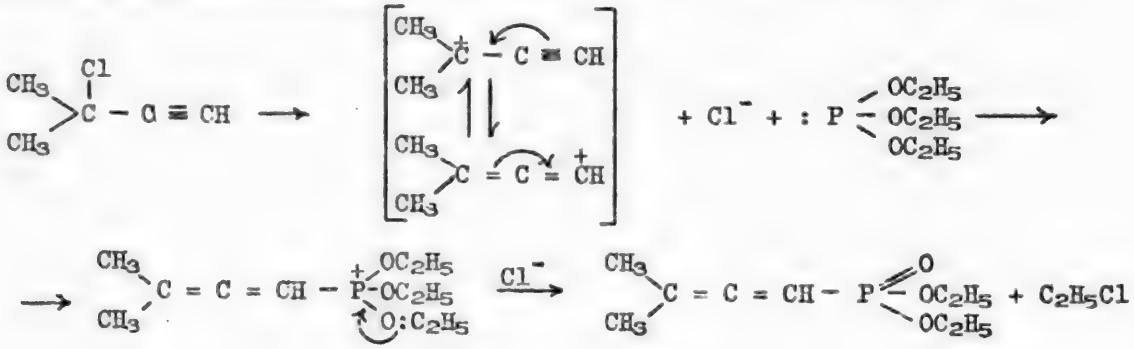
have become in most cases considerably clearer. We carried out the reactions between the acetylene chloride, 2-chloro-2-methylbutine-3, and the esters of phosphorous acid according to the method of Academician A.E.Arbuzov [5], by heating the reagents in sealed tubes. The end of the reaction was determined by a cessation in the change in volume of the reaction mixture.

From the reaction of triethylphosphite with 2-chloro-2-methylbutine-3, the chief product obtained had a b.p. of 183-185° at 6 mm; n_D^{20} 1.4598; d_4^{20} 1.1171; it was a thick, light-yellow liquid. There was also a small quantity of low-boiling fraction. Analysis of the product obtained for C, H, and P gave an empirical formula close to $C_{15}H_{32}O_8P_2$. The product was soluble in water, and could be separated from the solution unchanged. Upon heating with water in a sealed tube at 140°, for 3 hours, it was still unchanged. The product did not react with copper monohalides or with ethyl iodide upon heating. From the following data, we drew the conclusion that there was no trivalent phosphorus atom in the product. Saponification of the product with concentrated hydrochloric acid gave an acid in the form of a viscous liquid which did not crystallize upon standing. During the saponification, it was found that ethyl chloride was formed, in a quantity corresponding exactly to the two diethylphosphone groups in the product. Titration of the acid with a solution of caustic soda and analysis of its barium salt also corresponded to the presence in the product of two diethylphosphone groups.

An elementary analysis of the product, the results of titration of the acid, and the analysis of its barium salt, as well as consideration of its properties, all led to the conclusion that the substance obtained was apparently a secondary product of the reaction of the acetylene chloride and triethyl phosphite. In order to isolate the primary product of the reaction, we carried out the experiments on the reaction of the chloride with triethyl phosphite under less stringent conditions: at lower temperatures, with an excess of chloride, and in the presence of an inert solvent.

But when the temperature of the reaction was lowered from 150-160° to 120°, the reaction still formed chiefly the product noted above, with b.p. 185° at 7 mm; at 90°, practically no reaction at all took place. Upon carrying out the reaction in benzene solution at 130°, in addition to the product with b.p. 185° at 7 mm., we succeeded in isolating another substance with b.p. 120-122° at 10 mm, n_D^{20} 1.4555; d_4^{20} 1.0237.

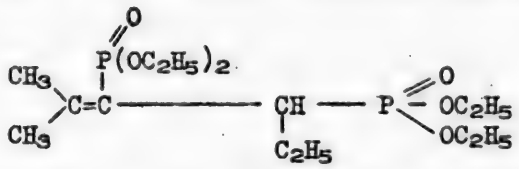
Elementary analysis of this latter product for carbon, hydrogen and phosphorus led to the empirical formula $C_8H_{17}O_3P$, corresponding to methyl-(diethylphosphone)-butine, or its isomer. As the product obtained gave no precipitate with an ammoniacal solution of silver oxice or copper oxide, it was possible to draw the conclusion that it had the allene structure, and consequently, that the reaction between the acetylene chloride and triethyl phosphite took place with a complete acetylene-allene rearrangement:



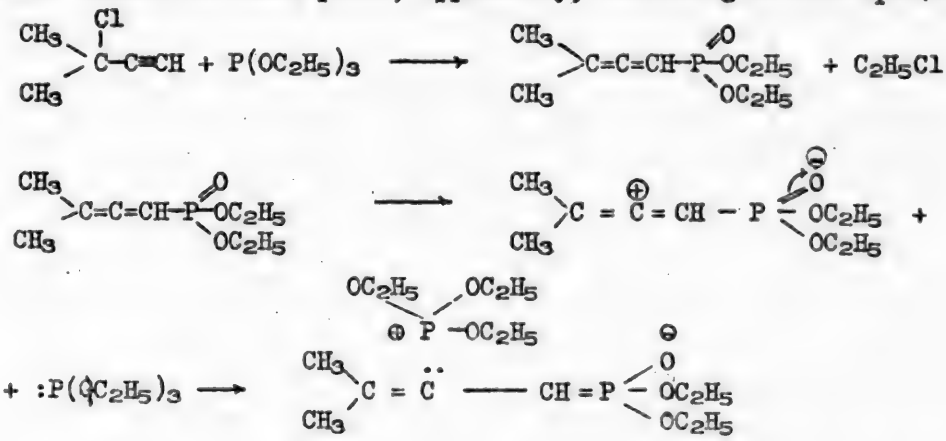
This acetylene chloride was stable at 130°; upon heating for 6 hours, no change in its constants was noted, and no isomerization. Upon heating the 2-methyl-4-diethylphosphonebutadiene-2,3 obtained to 150-160°, it was converted into the dimer with b.p. 205-206° at 5 mm; n_D^{20} 1.4795; d_4^{20} 1.0992, and this also served to confirm the correctness of its structural formula as an allene derivative.

To complete our elucidation of the structure of the above-mentioned compound with b.p. 185° at 7 mm, we carried out a reaction between 2-methyl-4-diethylphosphonebutadiene-2,3 and triethyl phosphite at 150°. We obtained as a result a product with b.p. 187-188° at 8 mm, n_D^{20} 1.4580, d_4^{20} 1.1166, i.e., according to its constants it was identical with the product obtained by the direct action of triethyl phosphite upon the acetylene chloride. As a result of oxidation of the product with potassium permanganate in aqueous solution, acetone could be identified in the form of its dinitrophenylhydrazone.

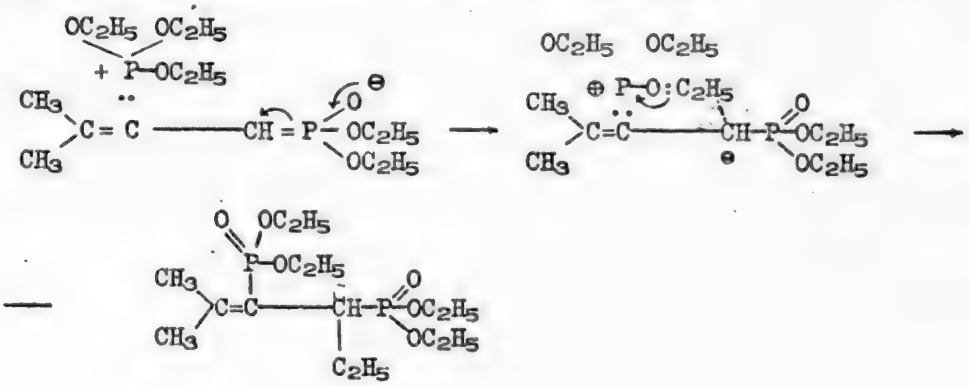
On the basis of the data obtained, we can conclude that the product with b.p. 185° at 7 mm is 2-methyl-3,4-di-(diethylphosphone)-hexene-2:



and that its formation takes place, apparently, according to the equations:



The addition product formed undergoes an internal rearrangement with an ethyl group transferring to the carbon atom in the β position to the phosphorous atom, and 2-methyl-3,4-di-(diethylphosphone)-hexene-2 is formed.



The action of triethyl phosphite on the allene chloride, 2-methyl-4-chlorobutadiene-2,3, with heating, did not lead to the isolation of any definite products. The reactions of tributyl phosphite and trimethyl phosphite with the acetylene chloride took place like the reaction of triethyl phosphite with the same chloride, although less smoothly.

In the two cases, the reaction gave a small quantity of the corresponding 2-methyl-4-dimethylphosphonebutadiene-2,3 with b.p. 131-132° at 4 mm, n_D^{20} 1.4310 d_4^{20} 0.9594; 2-methyl-4-dimethylphosphonebutadiene-2,3 with b.p. 117 at 10 mm; n_D^{20} 1.4632, d_4^{20} 1.0852, and high-boiling products corresponding to 2-methyl-3,4-di-(dibutylphosphone)-hexene-2, with b.p. 207-210° at 3 mm, n_D^{20} 1.4612; d_4^{20} 1.0505, and 2-methyl-3,4-di-(dimethylphosphone)-hexene-2 with b.p. 180-182° at 6 mm, n_D^{20} 1.4782; d_4^{20} 1.2218, as well as small quantities of high- and low-boiling fractions.

The reaction between sodium diethylphosphite and the acetylene chloride proceeded in a complicated manner; a mixture of products was obtained, boiling in the interval from 115-186° at 7 mm. No definite product could be separated from it.

EXPERIMENTAL

Action of Triethyl Phosphite on 2-Methyl-Chlorobutine-3

Experiment 1. 10 g of 2-methyl-2-chlorobutine-3 obtained by the method of T.A.Favorsky, and 16 g of triethyl phosphite were heated in a sealed tube at 150° for 10 hours. A diminution of the volume of the reaction mixture was noted; upon further heating, the volume underwent no further change. When the tube was opened, there was moderate pressure inside, as a result of the formation in the reaction of ethyl chloride. After the ethyl chloride had been removed by gentle heating, the reaction mixture was fractionated in vacuum from a small flask with a Widmer dephlegmator. After several distillations, 2.6 g of a fraction was obtained which boiled from 80 to 185° at 13 mm, and 7.5 g of 2-methyl-3,4-di-(diethylphosphone)-hexene-2.

B.p. 183-185° at 6 mm; 177-178° at 4 mm; n_D^{20} 1.4598; d_4^{20} 1.1171.
0.1060 g substance: 0.1871 g CO_2; 0.0788 g H_2O.
0.1676 g substance: 48.4 ml NaOH (T 0.02136).
Found %: C 47.87; H 8.21; P 17.00.
$C_{15}H_{32}O_8P_2$. Calculated %: C 48.64; H 8.64; P 16.80.

About 1 g of a fraction with b.p. 185-237° and 8.7 g of a tarry residue were obtained.

A repetition of the experiment with larger quantities of reagents gave similar results.

Experiment 2. The reaction was carried out with a twofold excess of chloride at a temperature of 130-140°. 20 g of chloride and 16 g of triethyl phosphite were heated at this temperature for 10 hours. Fractional distillation of the reaction mixture in vacuum (after removal of the ethyl chloride) gave 11.2 g of the original chloride with b.p. 74-78°, 3.1 g of a fraction boiling within the range 81-125° at 7 mm, 9 g of 2-methyl-3,4-di-(diethylphosphone)-hexene-2 with b.p. 185° at 7 mm, n_D^{20} 1.4610 and about 8 g of residue.

Experiment 3. The reaction with equimolecular quantities of reagents was carried out at 90° for 10 hours. Fractional distillation of the reaction mixture gave only the original materials.

Experiment 4. 9 g of the chloride, 14 g of triethylphosphite, and 17 g of absolute benzene were heated in a sealed tube at 130° for 6 hours. After removal of the benzene by distillation, fractionation of the reaction mixture gave 3.1 g of 2-methyl-4-diethylphosphonebutadiene-2,3: *

* During analysis of the compounds obtained by combustion in a small boat, a black colored melt was formed which did not decompose even upon strong and long-continued heating of the tube.

B.p. 120-122° at 10 mm; n_D^{20} 1.4555; d_4^{20} 1.0237.

0.1283 g substance: 0.2460 g CO_2; 0.0966 g H_2O.
0.1476 g substance: 36.8 ml NaOH (T 0.02136).
Found %: C 52.29; H 8.36; P 14.8.
$C_8H_{17}O_3P$. Calculated %: C 52.94; H 8.33; P 15.2.

5.9 g of 2-methyl-3,4-di-(diethylphosphone)-hexene-2 with b.p. 189° at 10 mm, n_D^{20} 1.4590, and about 6 g of residue were obtained.

The 2-methyl-4-diethylphosphonebutadiene-2,3 did not give a precipitate upon the addition of an ammoriacal solution of silver oxide or copper oxide.

Experiments on Heating 2-Methyl-2-chlorobutine-3

12 g of the acetylene chloride with b.p. 74-79° and n_D^{20} 1.4210 was heated in a sealed tube at 130° for 6 hours. Upon opening the tube after cooling, no pressure was observed. The index of refraction of the liquid was 1.4210. By fractional distillation of the liquid, 11.2 g of the original chloride was obtained.

Investigation of 2-Methyl-3,4-di-(diethylphosphone)-hexene-2

1. The action of water. a) 10 g of the product was dissolved in water and the solution obtained was distilled in vacuum. Water came over first, and then the unchanged product.

b) 4 g of 2-methyl-3,4-di-(diethylphosphone)-hexene-2 and 0.45 g of water were heated in a sealed tube for 3 hours at 140°. Fractional distillation of the reaction mixture gave 3.2 g of the original product.

2. The action of ethyl iodide. 6 g of 2-methyl-3,4-di-(diethylphosphone)-hexene-2 and 6 g of ethyl iodide were heated for 3 hours at 140°. Fractional distillation of the mixture gave the original reagents, unchanged.

3. The action of cuprous iodide. Upon the addition of cuprous iodide to 2-methyl-3,4-di(diethylphosphone)-hexene-2, there was no change in the temperature of the reaction mixture. No reaction at all was observed upon heating; the cuprous iodide did not dissolve in the product.

4. Saponification of 2-methyl-3,4-di-(diethylphosphone)-hexene-2. 6.2 g of the product was heated with 20 ml of concentrated hydrochloric acid in a sealed tube for 6 hours at 160°. After cooling, there appeared on the surface of the water layer a considerable layer of ethyl chloride. The tube was weighed before opening, and after it had been opened and moderately heated; the weight of the ethyl chloride formed was thus found to be 4.30 g. Theoretically, the saponification of the two phosphone groups should give 4.29 g of ethyl chloride. The aqueous solution was greatly concentrated, with the periodic addition of distilled water and thorough boiling with animal charcoal. The aqueous solution of acid was titrated with NaOH solution. The amount of solid alkali used for titration was 2.3 g; a theoretical calculation gave a requirement of 2.6 g. Upon the addition of barium chloride to the neutral solution, the barium salt precipitated. This was carefully washed with distilled water.

1.0824 g substance: 1.049 g $BaSO_4$.
Found %: Ba 57.0.
$C_7H_{12}O_8P_2Ba_2$. Calculated %: Ba 58.7.

5. Oxidation of 2-methyl-3,4-di-(diethylphosphone)-hexene-2. Into 5 g of the product, dissolved in 200 ml of water, 3 g of powdered potassium permanganate was gradually sprinkled, while the solution was cooled with running water. After the end of the reaction, the manganese dioxide was filtered off. From the filtrate, 20 ml of distillate was obtained; this was added to an alcoholic solution of dinitrophenylhydrazine. A dinitrophenylhydrazone was precipitated, with m.p. 124-126°.

The dinitrophenylhydrazone obtained from acetone and dinitrophenylhydrazine, had m.p. 125-127°. A mixed test gave no depression of the melting point.

The Behavior of 2-Methyl-4-diethylphosphonebutadiene-2,3 upon Heating

1.5 g of 2-methyl-4-diethylphosphonebutadiene-2,3 was heated in a small sealed tube for 7 hours at 150-160°. Fractional distillation of the reaction mixture gave 0.4 g of a fraction with b.p. 97-120° at 5 mm; n_D^{20} 1.4490, and 0.7 g of the dimer of 2-methyl-4-dimethylphosphonebutadiene-2,3:

B.p. 205-206° at 5 mm; n_D^{20} 1.4795 d_4^{20} 1.0992.

0.1104 g substance: 32.3 ml NaOH (T 0.01848).

Found %: P 15.0.

$C_{18}H_{34}O_6P_2$. Calculated %: P 15.2.

The Action of Triethyl Phosphite on 2-Methyl-4-diethylphosphonebutadiene-2,3

A mixture of 3 g of 2-methyl-4-diethylphosphonebutadiene-2,3 and 5 g of triethylphosphite was heated in a small sealed tube at 140° for 10 hours. Fractional distillation of the reaction mixture gave about 2 g of triethyl phosphite, 3 g of a fraction with b.p. 45-190° at 9 mm, and 1.3 g of a product with:

B.p. 187-188° at 8 mm; n_D^{20} 1.4580; d_4^{20} 1.1166.

0.0996 g substance: 33.1 ml NaOH (T 0.01848).

Found %: P 17.0.

$C_{15}H_{32}O_6P_2$. Calculated %: P 16.8.

The Action of Triethyl Phosphite on the Allyl Chloride — 2-Methyl-4-chlorobutadiene-2,3

10 g of the chloride and 16 g of triethylphosphite were heated in a sealed tube for 10 hours at 150°. Fractional distillation of the reaction mixture gave a large quantity of ethyl chloride (floating above water), then 8.5 g of a fraction with b.p. 22-78° at 19 mm; n_D^{20} 1.4176 and 7.5 g with b.p. 78-85° at 16 mm, n_D^{20} 1.4320. There was 4.5 g residue from the distillation. Further fractional distillation of the fraction with b.p. 22-78° at 19 mm gave mostly the original triethyl phosphite; fractional distillation of the last fraction gave another fraction with b.p. 67-70° at 11 mm, n_D^{20} 1.4280. This was not investigated further.

The Action of Tributyl Phosphite on 2-Methyl-2-chlorobutine-3

50 g of tributyl phosphite and 20 g of 2-methyl-2-chlorobutine-3 were heated in a sealed tube for 10 hours at 150°. Distillation of the reaction mixture gave the following fractions:

1) B.p. 75-80° at 760 mm; n_D^{20} 1.4060 — 13.8 g.
2) B.p. 110-130° at 6 mm; n_D^{20} 1.4372 — 3.4 g.
3) B.p. 133-140° at 6 mm; n_D^{20} 1.4374 — 4.6 g.
4) B.p. 140-235° at 7 mm; n_D^{20} 1.4525 — 2.3 g.
5) B.p. 205-221° at 2 mm; n_D^{20} 1.4593 — 17.6 g.
6) B.p. 221-226° at 2 mm; n_D^{20} 1.4600 — 4.2 g.

Residue..... 16.4 g.

Fractional distillation of the first fraction gave 12 g of butyl chloride with b.p. 76-78° at 760 mm, n_D^{20} 1.4052; the second and third fractions gave 2.3 g of the

original tributyl phosphite and 4.3 g of 2-methyl-4-dibutylphosphonebutadiene-2,3:*

B.p. 131-132° at 4 mm; n_D^{20} 1.4310; d_4^{20} 0.9594.
0.1272 g substance: 27.6 ml NaOH (T 0.01848).
Found %: P 11.1.
$C_{13}H_{25}O_3P$. Calculated %: P 11.8.

The product gave no precipitate with an ammoniacal solution of silver and copper oxides. Distillation of the fourth, fifth and sixth fractions gave 4.3 g of a fraction with b.p. 145-203° at 3 mm, n_D^{20} 1.4580, and 14.5 g of 2-methyl-3,4-di--(dibutylphosphone)-hexene-2:*

B.p. 207-210° at 3 mm; n_D^{20} 1.4612; d_4^{20} 1.0505.
0.1142 g substance: 24.2 ml NaOH (T 0.02145).
Found %: P 12.6.
$C_{23}H_{48}O_6P_2$. Calculated %: P 12.2.

In addition about 3 g of a fraction was obtained with b.p. 210-227° at 3 mm, n_D^{20} 1.4652.

The Action of Trimethyl Phosphite on 2-Methyl-2-chlorobutine-3.

15 g of 2-methyl-2-chlorobutine-3, 20 g of trimethyl phosphite, and 20 g of benzene were heated in a sealed tube for 8 hours at 120°. Pressure was noted when the tube was opened. After removal from the reaction mixture of the methyl chloride (floating on water) and the benzene, the residue was distilled in vacuum. There were obtained 13.6 g of a fraction boiling in the range 80-110° at 14 mm, n_D^{20} 1.4310; 7.6 g of a fraction with b.p. 110-135° at 14 mm; n_D^{20} 1.4615; 16.1 g with b.p. 201-210 at 14 mm, n_D^{20} 1.4730, and 4.1 g of residue. Distillation of the first fraction gave 9.8 g of the methyl ester of methylphosphinic acid with b.p. 70° at 10 mm, n_D^{20} 1.4112. Distillation of the second fraction gave 3.1 g of 2-methyl-4-dimethylphosphonebutadiene-2,3, which formed no precipitate with an ammoniacal solution of silver oxide:

B.p. 117° at 10 mm; n_D^{20} 1.4682; d_4^{20} 1.0852.
0.1052 g substance: 28.5 ml NaOH (T 0.02458).
Found %: P 18.5.
$C_7H_{13}O_3P$. Calculated %: P 17.6.

Distillation of the third fraction gave 9.6 g of 2-methyl-3,4-di-(dimethylphosphone)-hexene-2:

B.p. 180-182° at 6 mm; n_D^{20} 1.4782; d_4^{20} 1.2218.
0.1454 g substance: 57.2 ml NaOH (T 0.01848).
Found %: P 20.2.
$C_{10}H_{22}O_6P_2$. Calculated %: P 20.6.

In addition, there were small quantities of low- and high-boiling fractions.

The Action of Sodium Diethylphosphite on 2-Methyl-2-chlorobutine-3

An ether solution of sodium diethylphosphite was prepared from 27 g of diethylphosphorous acid and 4.5 g of sodium in 80 ml of absolute ether. To the solution obtained, 20 g of 2-methyl-2-chlorobutine-3 was gradually added. The evolution of heat was noted in the reaction mixture, but no precipitate of sodium chloride was observed. After the ether layer had been dried and the ether distilled off, the residue was fractionated in vacuum. The distillation gave a small fraction, boiling within the range 115-186° at 7 mm. A second distillation gave a fraction (3.4 g) which boiled from 182-186° at 7 mm, n_D^{20} 1.4685, and had a phosphorus content of

*Analysis for carbon and hydrogen could not be carried out because of the formation of a melt.

14.8%. This, however, was not investigated further.

SUMMARY

1. The action of the following esters of phosphorous acid: triethyl phosphite, tributyl phosphite, and trimethyl phosphite, on 2-methyl-2-chlorobutine-3 has been investigated.

The reactions take place with an acetylene-allene rearrangement to give a quantity of primary reaction products corresponding to 2-methyl-4-dialkylphosphonebutadiene-2,3. In addition, 2-methyl-3,4-di(dialkylphosphone)-hexene-2 is formed by the further actinn of the phosphorous esters on 2-methyl-4-dialkylphosphonebutadiene-2,3.

2. The structure of 2-methyl-3,4-di(diethylphosphone)-hexene-2 has been demonstrated, and a mechanism has been suggested for its formation.

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ALKOXYISOPROPYL ESTERS OF PHOSPHOROUS ACID AND THEIR PROPERTIES

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In a previous paper [1] we described the tri-β-methoxy- and tri-β-ethoxyethyl esters of phosphorous acid. The alkoxyethyl esters of phosphorous acid obtained by the action of the corresponding halogen-substituted ethers underwent isomerization and conversion into di-β-methoxy- and di-β-ethoxy ethyl esters of β-alkoxyethylphosphinic acids. The esters also reacted with bromomethyl ethers to give di-β-methoxy- and di-β-ethoxyethyl esters of alkoxymethylphosphinic acids.

In the present paper we report on the continuation of the investigation of alkoxy-substituted esters of phosphorous acid. As initial products, we used: the primary monoethyl ether of propylene glycol, and the primary monoisopropyl ether of propylene glycol. These cellosolves were obtained by the alcoholization of propylene oxide in the presence of caustic soda; this, according to the investigations of Chitwood and Freure [2], leads to the formation of primary ethers of propylene glycol.

Tri-β-ethoxy- and tri-β-isopropoxyisopropyl esters of phosphorous acid were obtained according to Milobedzki and Sachnovski [3], as altered by K.V.Nikonorov, by the action of phosphorous trichloride on the corresponding cellosolve in the presence of freshly distilled dimethylaniline, in absolute dry ether as a solvent. The reaction can be indicated by the equation:

$$3CH_3-\underset{\underset{OH}{|}}{CH}-CH_2OR' + PCl_3 + 3C_6H_5N(CH_3)_2 = \left(\begin{matrix}CH_3\\ ROCH_2\end{matrix}\!\!>\!CHO\right)_3P + 3C_6H_5N(CH_3)_2 \cdot HCl,$$

where R is ethyl or isopropyl respectively. Tri-β-ethoxy- and tri β-isopropoxyisopropyl esters of phosphorous acid appear as colorless, fluid liquids with a weak odor reminiscent of the odors of phosphites. The esters react with cuprous iodide and gave a rise in temperature from 20° to 41° on being mixed with it, but no crystalline derivatives could be obtained. Upon continued standing, no products of reaction crystallized.

The tri-β-ethoxyisopropyl ester of phosphorous acid is isomerized by the action of ethyl-β-bromopropyl ether to give the di-β-ethoxyisopropyl ester of β-ethoxyisopropylphosphinic acid. The isomerization of the esters of phosphorous acid was thoroughly investigated earlier by Acad. A.E.Arbuzov.

The tri-β-ethoxyisopropyl ester of phosphorous acid reacts with halogen-substituted ethers to form ethers of alkoxymethylphosphinic acids. We studied the action of monobromomethyl, bromomethylethyl, bromomethylpropyl, and chloromethylbutyl ethers.

The course of isomerization and the action of halogen-substituted ethers can be described by the equations:

$$\left(C_2H_5OCH_2\overset{CH_3}{\underset{}{>}}CHO\right)_3P + BrCH_2OR = \left(C_2H_5OCH_2\overset{CH_3}{\underset{}{>}}CHO\right)_3P\overset{CH_2OR}{\underset{Br}{<}},$$

$$\left(C_2H_5OCH_2\overset{CH_3}{\underset{}{>}}CHO\right)_2\!=\!P\!-\!O\!-\!\underset{C_2H_5OCH_2}{\overset{CH_3}{\underset{}{>}}}CH\!-\!CH_2OR \quad (Br) = \left(C_2H_5OCH_2\overset{CH_3}{\underset{}{>}}CHO\right)_2P\overset{CH_2OR}{\underset{O}{<}} +$$

$$+ C_2H_5OCH_2CHBrCH_3.$$

The di-β-ethoxyisopropyl esters of alkoxymethylphosphinic acids obtained were colorless, odorless liquids.

We made attempts to obtain tri-β-phenoxyethyl ester of phosphorous acid from the monophenyl ether of ethylene glycol and phosphorus trichloride in the presence of freshly distilled dimethylaniline. The reaction took place as usual with the separation of dimethylaniline hydrochloride. It was necessary to assume that the tri-β-phenoxyethyl ester of phosphorous acid was also formed. However, upon distillation of the products of reaction in vacuum, it appeared impossible to isolate any definite fraction. During distillation, decomposition took place, and increased considerably. During the decomposition, some substance distilled over unchanged. The residue in the flask was changed into a thick, viscous, orange-colored mass, obviously containing phosphorus which had separated out. The distilled substance partially crystallized to give colorless crystals; investigation indicated the presence of phenol, as was indicated by the odor, the violet color with ferric chloride, and the formation of tribromophenol with m.p. 94°. The liquid portion reacted with cuprous iodide, giving a rise in temperature from 25 to 35°; this doubtless indicated the presence of the tri-β-phenoxyethyl ester of phosphorous acid, or the presence of compounds of trivalent phosphorus in general. The liquid part of the distillate again underwent decomposition upon distillation. During decomposition, obviously, phenol is split off, and a vinyl ester of phosphorous acid or a mixed vinyl-β-phenoxyethyl ester of phosphorous acid is formed, which polymerizes under the conditions of the distillation: $(C_6H_5OCH_2CH_2O)_3P \longrightarrow$ $\longrightarrow C_6H_5OH + (CH_2{=}CHO)_3P$ or $CH_2 = CHOP(OCH_2CH_2OC_6H_5)_2$. The action of phosphorus trichloride on the primary monoethyl ether of propylene glycol gave di-β-ethoxyisopropylphosphorous acid according to the equation:

$$3C_2H_5OCH_2\overset{CH_3}{\underset{}{>}}CHOH + PCl_3 = \left(C_2H_5OCH_2\overset{CH_3}{\underset{}{>}}CHO\right)_2POH +$$

$$+ C_2H_5OCH_2CHClCH_3 + 2HCl.$$

The di-β-ethoxyisopropylphosphorous acid was a colorless, odorless liquid. From the action of phosphorus trichloride on the phenyl ether of ethylene glycol, the formation of di-β-phenoxyethylphosphorous acid was to be expected:

$$3C_6H_5OCH_2CH_2OH + PCl_3 = (C_6H_5OCH_2CH_2O)_2POH + C_6H_5OCH_2CH_2Cl + 2HCl.$$

Distillation of the products of reaction gave fractions which corresponded, according to data in the literature, to β-chloroethylphenyl ether. Yield, 100% of theory. The β-chloroethylphenyl ether was subjected to reaction in accordancewith the equation above.

The residue, obviously consisting of di-β-phenoxyethylphosphorous acid, upon distillation in vacuum, decomposed as did the tri-β-phenoxyethyl ester of phosphorous acid. The fraction driven off appeared to be phenol, judging from its odor, violet coloration with ferric chloride, and the formation of tribromophenol with m.p. 94°. A thick orange-colored mass remained in the flask; this probably

consisted of polymers of divinyl- or vinylphosphorous acid:

$$(C_6H_5OCH_2CH_2O)_2POH \longrightarrow C_6H_5OH + (CH_2{=}CHO)_2PUH \text{ or}$$

$$CH_2{=}CHO{-}\underset{\underset{O}{\parallel}}{\overset{\overset{H}{|}}{P}}{-}OCH_2CH_2O{-}C_6H_5$$

Attempts to obtain the silver salt of the crude di-β-phenoxyethylphosphorous acid were not crowned with success.

The action of phosphorus trichloride on the phenyl ether of ethylene glycol, according to N.A.Menshutkin [4], gives the di-acid chloride of phenoxyethylphosphorous acid, a colorless liquid which fumes in air.

EXPERIMENTAL

The Formation of the Tri-β-Ethoxyisopropyl Ester of Phosphorous Acid

The ester of phosphorous acid was obtained from the primary monoethyl ether of propylene glycol, which was obtained from absolute ethyl alcohol and propylene oxide in the presence of caustic soda [2], and after two consecutive fractionations in a column with a glass cap had b.p. 130-131°, n_D^{20} 1.4054, d_4^{20} 0.894.

Into a round-bottomed flask, fitted with a reflux condenser, a dropping funnel, and a stirrer, were placed 90 g of the primary monoethyl ether of propylene glycol, 105 g of freshly distilled dimethyl aniline, and 300 ml of dry ether. The mixture was cooled with snow and vigorously shaken, while from the dropping funnel 39 g of phosphorus trichloride was gradually allowed to flow in. After it was all added, the stirrer was kept going for another half hour. The precipitate of dimethylaniline hydrochloride was filtered off and washed with dry ether. The ethyl ether was removed by distillation on the water bath, and the residue distilled in vacuum. After two consecutive fractionations, a fraction was obtained with b.p. 156-158° at 9 mm.

Yield of ether 68 g, or 70% of theory.

n_D^{20} 1.4320; d_4^{20} 0.983; MR_D 89.4; $C_{15}H_{33}O_6P$. Calculated: MR_D 89.5.

0.2792 g substance: 31.7 ml NaOH (T 0.2843)* (according to Neymann)**
0.1656 g substance: 19.4 ml NaOH (T 0.2843).
Found %: P 8.93, 9.05.
$C_{15}H_{33}O_6P$. Calculated %: P 9.11.

The Action of Cuprous Iodide on the Tri-β-ethoxyisopropyl Ester of Phosphorous Acid

To a test tube was added at the same time 2 g of the ether and the calculated quantity of cuprous iodide. The cuprous iodide reacted with the ether with the evolution of heat. The temperature of the reacting substances rose from 19 to 41°. Then the test tube was heated until the copper salt was almost completely dissolved. The products of reaction were treated with water to remove cuprous iodide and then extracted with ether. Upon evaporation of the ether, there remained a syrupy, transparent liquid, which did not crystallize upon prolonged standing.

The Isomerization of the Tri-β-ethoxyisopropyl Ester of Phosphorous Acid Under the Action of Ethyl-β-bromopropyl Ether

5.3 g of the tri-β-ethoxyisopropyl ester of phosphorous acid and 0.65 g of ethyl-β-bromopropyl ether were sealed in a tube*** which had a constriction to permit

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*Neymann,Z. physiol. 37,129 (1902); 43,35 (1904).

**1 ml of this solution corresponded to 0.000786 g of phosphorus.

***Dissertation of A. E. Arbuzov, 1914.

better observation of the change in volume. The tube was heated at 120° for 9 hours, at which time no further change in volume took place. The contents of the tube were distilled in vacuum. Two consecutive fractionations gave a fraction with b.p. 162-164° and the constants:

n_D^{20} 1.4320; d_4^{20} 1.012; MR_D 87.14; $C_{15}H_{33}O_6P$. Calculated MR_D 86.17.

The Formation of Ethyl-β-bromopropyl Ether

Ethyl-β-bromopropyl ether was obtained by the action of phosphorous tribromide on the primary monoethyl ether of propylene glycol. In a flask fitted with a reflux condenser, 15 g of the primary monoethyl ether of propylene glycol was placed, and 13 g of phosphorus tribromide was cautiously added. After all the tribromide had been added, the flask was heated on an oil bath. The reaction products were distilled in vacuum. Two consecutive fractionations gave 11 g of a fraction with b.p. 32-34° at 10 mm and the constants:

n_D^{20} 1.4410; d_4^{20} 1.243; MR_D 35.26; $C_5H_{11}OBr$. Calculated MR_D 34.7.

The Action of Monobromomethyl Ether on the Tri-β-ethoxyisopropyl Ester of Phosphorous Acid

The reaction of halogen-substituted ethers with the tri-β-ethoxyisopropyl ester of phosphorous acid was carried out in a round-bottomed flask fitted with a reflux condenser and a dropping funnel. To 10 g of the tri-β-ethoxyisopropyl ester of phosphorous acid, 3.7 g of monobromomethyl ether was gradually added. The reaction took place with the evolution of heat. In order to complete the reaction, the mixture was heated as usual on an oil bath at a temperature of 120° for 1 to 2 hours. The reaction products were distilled in vacuum. Two consecutive fractionations gave 4.8 g of a fraction with b.p. 165-168° at 16 mm, and the constants:

n_D^{20} 1.4272; d_4^{20} 1.049; MR_D 72.71; $C_{12}H_{27}O_6P$. Calculated MR_D 72.90.

0.1724 g substance: 23.4 ml NaOH (T 0.02843).
0.1298 g substance: 17.1 ml NaOH (T 0.02483).
Found %: P 10.5, 10.3.
$C_{12}H_{27}O_6P$. Calculated %: P 10.39.

The Action of Bromomethylethyl Ether on the Tri-β-ethoxyisopropyl Ester of Phosphorous Acid

To 10 g of the tri-β-ethoxyisopropyl ester of phosphorous acid, 4 g of bromomethylethyl ether was gradually added. After heating, the reaction products were distilled under vacuum. 3.9 g of a fraction with b.p. 164-166° at 7 mm was obtained.

n_D^{20} 1.4312; d_4^{20} 1.040; MR_D 77.45; $C_{13}H_{29}O_6P$. Calculated MR_D 77.52.

0.1201 g substance: 15.6 ml NaOH (T 0.02843).
0.1234 g substance: 16.0 ml NaOH (T 0.02843).
Found %: P 10.2, 10.11.
$C_{13}H_{29}O_6P$. Calculated %: P 9.9.

The Action of Bromomethylisopropyl Ether on the Tri-β-ethoxyisopropyl Ester of Phosphorous Acid

To 7 g of the tri-β-ethoxyisopropyl ester of phosphorous acid, 3.1 g of bromomethylisopropyl ether was gradually added. After two distillations, the products of reaction gave 4.5 g of a fraction with b.p. 158-160° at 6 mm, and the constants:

n_D^{20} 1.4310; d_4^{20} 1.029; MR_D 82.02; $C_{14}H_{31}O_6P$. Calculated MR_D 82.14.

0.1018 g substance: 11.7 ml NaOH (T 0.02843).
0.1380 g substance: 15.8 ml NaOH (T 0.02843).
Found %: P 9.02, 8.99.
$C_{14}H_{31}O_6P$. Calculated %: P 9.5.

The Action of Chloromethylbutyl Ether on the Tri-β-ethoxyisopropyl Ester of Phosphorous Acid

To 7 g of the tri-β-ethoxyisopropyl ester of phosphprous acid, 2.5 g of chloromethylbutyl ether was gradually added. The products of reaction were heated on an oil bath, and then distilled in vacuum. Two fractionations gave a fraction with b.p. 210-213° at 35 mm, and the constants:

n_D^{20} 1.4309; d_4^{20} 1.013; MR_D 86.62; $C_{15}H_{33}O_6P$. Calculated: MR_D 86.76.

0.1170 g substance: 11.6 ml NaOH (T 0.02843).
0.1714 g substance: 12.1 ml NaOH (T 0.02843).
Found %: P 7.8, 7.98.
$C_{15}H_{33}O_6P$. Calculated %: P 8.1.

Formation of the Tri-β-isopropoxyisopropyl Ester of Phosphorous Acid

The primary isopropyl ether of propylene glycol was obtained from isopropyl alcohol and propylene oxide in the presence of caustic soda [2]. Fractionation carried out in a column with a glass cap gave a fraction with b.p. 137-138° and the constants: n_D^{20} 1.4070, d_4^{20} 0.879, in accordance with the literature data.

The tri-β-isopropoxyisopropyl ester of phosphorous acid was obtained in the same way as the tri-β-ethoxyisopropyl ester. For the reaction 50 g of the primary isopropyl ether of propylene glycol was taken, along with 51.2 g of freshly distilled dimethylaniline, and 150 ml of dry ether. The mixture was cooled and vigorously agitated, while 19.4 g of phosphorus trichloride was added. After the dimethylaniline hydrochloride had been removed, and the ether distilled off, the remaining products of the reaction were fractionated in vacuum. A fraction was obtained with b.p. 160-168° at 12 mm, to the amount of 18 g. This appeared to be impure. In a second experiment, 13 g of a similar fraction was obtained. The product of both experiments, to the total amount of 31 g, was treated with metallic sodium to remove acid esters. After fractionation of the distillate, the ester of phosphorous acid was obtained, with b.p. 152-155° at 10 mm and the constants:

n_D^{20} 1.4300; d_4^{20} 0.9515; MR_D 103.6; $C_{18}H_{39}O_6P$. Calculated MR_D 103.37.

0.1220 g substance: 12.8 ml NaOH (T 0.02843).
0.1032 g substance: 10.6 ml NaOH (T 0.02843).
Found %: P 8.24, 8.07.
$C_{18}H_{39}O_6P$. Calculated %: P 8.1.

The Formation of the Tri-β-phenoxyethyl Ester of Phosphorous Acid

The phenyl ether of ethylene glycol was obtained from technical chlorohydrin and sodium phenolate upon prolonged boiling. For purposes of synthesis, the fraction boiling from 118-121° at 15 mm was taken. In this experiment, 200 g of the phenyl ether of ethylene glycol, 164 g of freshly distilled dimethyl aniline, and 500 ml of dry ether were used. The mixture was cooled and stirred while 62.2 g of phosphorous trichloride was added. The dimethylaniline hydrochloride which formed was filtered off. The products of reaction were distilled in vacuum. The distillation took place with gradual, steady decomposition. Together with the products of decomposition, some phosphorous acid ester distilled over. The residue in the flask consisted of a thick, orange-colored mass. A second distillation of the fraction

gave similar results. The product of distillation crystallized in the condenser, and appeared to be phenol. It gave a violet color with ferric chloride. Upon bromination, it was converted into tribromophenol, with m.p. 94°. A mixed test gave no depression of the melting point. The various fractions reacted with cuprous iodide, giving a rise in the temperature of the reaction mixture. The maximum rise in temperature in any of the fractions was from 25 to 35°.

The Formation of Di-β-ethoxyisopropylphosphorous Acid

To 80 g of the primary ethyl ether of propylene glycol, there was gradually added, with stirring and cooling, 35.2 g of phosphorus trichloride. The hydrogen chloride formed was removed by a stream of dry air. The reaction products were fractionated under vacuum. After three consecutive fractionations, 25 g of a fraction was obtained with b.p. 135-137° at 9 mm, and the constants:

n_D^{20} 1.4270; d_4^{20} 1.049; MR_D 62.4; $C_{10}H_{23}O_5P$. Calculated MR_D 61.34.

0.1560 g substance: 24.3 ml NaOH (T 0.02843).
0.2710 g substance: 43.0 ml NaOH (T 0.02843).
Found %: P 12.24, 12.46.
$C_{10}H_{23}O_5P$. Calculated %: P 12.20.

The Formation of Di-β-phenoxyethylphosphorous Acid

To 100 g of the monophenyl ether of ethylene glycol, 33.2 g of phosphorus trichloride was added. The hydrogen chloride was removed by a stream of dry air. The products of reaction were fractionated in vacuum. A fraction was obtained with b.p. 90-93° at 4 mm and the constants:

n_D^{20} 1.5258; d_4^{20} 1.121; MR_D 42.47; $C_8H_9OClF_3$. Calculated MR_D 42.05.

These constants agreed with the data of the literature for β-chloroethylphenyl ether. Yield 40 g, or 100% of theory.

Upon further distillation of the residue, there was obviously a steady, gradual decomposition. The products of distillation partly crystallized. Under investigation, the crystals appeared to be phenol. They gave a violet color with ferric chloride and tribromophenol on bromination; m.p. 94°.

The residue was a viscous, orange-colored mass.

Attempts to obtain the silver salt from the residue after distilling off the β-chloroethylphenyl ether, in a separate experiment, gave no positive results. A salt was obtained by pouring a solution of silver nitrate into an aqueous solution of the residue containing a small amount of ammonia. The gray precipitate which formed quickly turned black.

The Formation of the Di-acid Chloride of β-phenoxyethylphosphorous Acid

The di-acid chloride of β-phenoxyethylphosphorous acid was obtained, according to the method of N.A.Menshutkin [4], by pouring 45 g of the monophenyl ether of ethylene glycol into 44.8 g of phosphorus trichloride, with mechanical stirring. The hydrogen chloride was removed by a stream of dry air. The residue was distilled, and after two consecutive fractionations, gave 24 g of a fraction with b.p. 150-152° at 9 mm, and the constants:

n_D^{20} 1.5437; d_4^{20} 1.328; MR_D 56.71; $C_8H_9O_2Cl_2PF_3$. Calculated MR_D 56.75.

0.1040 g substance: 16.8 ml NaOH (T 0.02181)
0.0986 g substance: 16.6 ml NaOH (T 0.02181)
Found %: P 12.7, 13.03.
$C_8H_9O_2Cl_2P$. Calculated %: P 12.97.

SUMMARY

1. The tri-β-ethoxyisopropyl and tri-β-isopropoxyisopropyl esters of phosphorous acid have been obtained and described.

2. The isomerization of the tri-β-ethoxyisopropyl ester of phosphorous acid has been carried out under the action of ethyl-β-bromopropyl ether to give the di-β-ethoxyisopropyl ester of β-ethoxyisopropylphosphinic acid.

3. A study has been made of the action of halogen-substituted ethers on the tri-β-ethoxyisopropyl ester of phosphorous acid. The following compounds have been obtained: the di-β-ethoxyisopropyl ester of methoxymethylphosphinic acid; the di-β-ethoxyisopropyl ester of ethoxymethylphosphinic acid; the di-β-ethoxyisopropyl ester of propoxymethylphosphinic acid; and the di-β-ethoxyisopropyl ester of butoxymethylphosphinic acid.

4. Di-β-ethoxyisopropylphosphorous acid has been obtained.

5. The di-acid chloride of β-phenoxyethylphosphorous acid has been obtained.

6. Attempts to obtain the tri-β-phenoxyethyl ester of phosphorous acid and to obtain di-β-phenoxyethylphosphorous acid did not give positive results. During their distillation, phenol split off, and the residue polymerized to give a tarry mass.

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*See CB translation p. 917 ff.

TIN-PHOSPHORO-ORGANIC COMPOUNDS

III. SYNTHESIS OF COMPOUNDS WITH PHENYL RADICALS ATTACHED TO THE PHOSPHORUS

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We have shown in preceding communications [1] the possibility of synthesizing compounds containing a phosphorus-tin bond by the action of organic tin derivatives with halogen atoms attached to the tin, upon the complete esters of phosphorous acid. Among the compounds used were the trialkyltin halides and the dialkyltin dihalides.

We did not succeed in obtaining phosphorus-tin compounds with phenyl radicals attached to the tin.

In the present communication, we present data on the synthesis and on some of the properties of tin-phosphoro-organic compounds containing phenyl radicals attached to the phosphorus.

We accomplished the synthesis of this type of compound by the action of alkyltin halides on the esters of phenylphosphinous and diphenylphosphinous acids.

Thus, the action of trialkyliodotin derivatives on the esters of phenylphosphinous acid gave esters of phenylphosphonetrialkyltin, according to the mechanism:

$$C_6H_5P(OR)_2 + ISnR'_3 = RI + C_6H_5 - \underset{\underset{OR}{|}}{\overset{\overset{O}{\|}}{P}} - SNR'_3$$

The compounds obtained in this fashion are listed in Table 1. They are in the form of colorless finely crystalline substances.

Similarly, by the action of dialkyldiiodotin compounds on the esters of phenylphosphinous acid, we obtained the esters of di-(phenylphosphone)-dialkyl tin.

The results of these experiments are summarized in Table 2. The compounds obtained are colorless and finely crystalline, insoluble in organic solvents. They were purified by washing with alcohol and ether.

The yields of diphosphone derivatives, as is obvious, were much higher than the yields of monophosphone derivatives.

Starting with the ester of diphenylphosphinous acid, we synthesized, by means of the action of trialkyliodotin derivatives, the oxides of trialkylstannylphosphines (cf Table 3):

$$(C_6H_5)_2P - OC_2H_5 + ISnR_3 = (C_6H_5)_2\underset{\underset{O}{\|}}{P} - SnR_3 + C_2H_5I.$$

The yields (Table 3) were small because of the action of the formed ethyl iodide upon the original ester of diphenylphosphinous acid, which transformed the greater part of the ester into the isomeric diphenylethylphosphine oxide:

$$(C_6H_5)_2P - OC_2H_5 + C_2H_5I = (C_6H_5)_2\underset{\underset{O}{\|}}{P} - C_2H_5 + C_2H_5I$$

TABLE 1

Original ester of phenylphosphinous acid	Original tin derivative	Compound synthesized	m.p.	Yield (%)
$C_6H_5P(OCH_3)_2$...	$(CH_3)_3SnI$	$C_6H_5P(O)(OCH_3)Sn(CH_3)_3$	132-134°	15.5
$C_6H_5P(OC_2H_5)_2$..	$(C_2H_5)_3SnI$	$C_6H_5P(O)(OC_2H_5)Sn(C_2H_5)_3$	294-297	13.0
$C_6H_5P(OC_2H_5)_2$..	$(n\text{-}C_4H_9)_3SnI$	$C_6H_5P(O)(OC_2H_5)Sn(n\text{-}C_4H_9)_3$	302-305	7.2

TABLE 2

Original ester of phenylphosphinous acid	Original tin derivative	Compound synthesized	m.p.	Yield (%)
$C_6H_5P(OCH_3)_2$	$(CH_3)_2SnI_2$	$(CH_3)_2Sn[P(O)(OCH_3)C_6H_5]_2$	291-293°	54.5
$C_6H_5P(OC_2H_5)_2$	$(C_2H_5)_2SnI_2$	$(C_2H_5)_2Sn[P(O)(OC_2H_5)C_6H_5]_2$	296-300°	33.5
$C_6H_5P(OC_3H_7\text{-}n)_2$	$(C_2H_5)_2SnI_2$	$(C_2H_5)_2Sn[P(O)(OC_3H_7)C_6H_5]_2$	245-248	61.4

TABLE 3

Original ester	Original tin derivative	Compound synthesized	m.p.	Yield (%)
$(C_6H_5)_2P - OC_2H_5$	$(CH_3)_3SnI$	$(C_6H_5)_2P(O)Sn(CH_3)_3$	365-368°	9.8
$(C_6H_5)_2P(O)OC_2H_5$	$(C_2H_5)_3SnI$	$(C_6H_5)P(O)Sn(C_2H_5)_3$	346-348	5.1

which was also isolated from the products of reaction. The compounds obtained were colorless crystalline substances, insoluble in the usual organic solvents. Because of the difficulty of purification, it was impossible to obtain good analytical results for them. Similarly, the action of the ethyl ester of diphenylphosphinous acid on dialkyldiiodotin gave a diphosphine oxide containing an atom of tin, according to the reaction:

$$2(C_6H_5)_2\overset{O}{\overset{\|}{P}} - OC_2H_5 + I_2SnR_2 = (C_6H_5)_2\overset{O}{\overset{\|}{P}} - \underset{R}{\overset{R}{Sn}} - \overset{O}{\overset{\|}{P}}(C_6H_5)_2 + 2C_2H_5I.$$

Results are listed in Table 4.

TABLE 4

Original ester	Original tin derivative	Compound synthesized	m.p.	Yield (%)
$(C_6H_5)_2P-OC_2H_5$	$(CH_3)_2SnI_2$	$\left[(C_6H_5)_2\overset{O}{\overset{\|}{P}}\right]_2Sn(CH_3)_2$	372-375°	26.6
$(C_6H_5)_2P-OC_2H_5$	$(C_2H_5)_2SnI_2$	$\left[(C_6H_5)_2\overset{O}{\overset{\|}{P}}\right]_2Sn(C_2H_5)_2$	351-353	17.3

The compounds obtained were finely crystalline colorless compounds, insoluble in the usual organic solvents.

The Chemical Properties of the Phenylphosphorotin Compounds Synthesized

As has been shown in preceding communications [1], the tin-phosphorus bond is unstable under the action of acids and alkalies. Even at room temperature, 5% hydrochloric acid breaks the tin-phosphorus bond.

An investigation of the chemical properties of the compounds described in the present communication confirms the instability of the tin-phosphorus bond that we found earlier, both in acids and in alkalies.

The esters of phenylphosphonetrialkyltin were stable to pure water and were unchanged upon boiling with water. At room temperature, 15% hydrochloric acid breaks the tin-phosphorus bond to form trialkylchlorotin. Caustic potash (10%) at room temperature breaks the tin-phosphorus bond to give a hydrate of trialkyltin oxide.

The esters of di-(phenylphosphone)-dialkyltin possess similar properties.

Boiling water does not act upon them, while 15% hydrochloric acid at room temperature leads to the formation of dialkyldichlorotin. At room temperature, chlorine breaks the tin-phosphorus bond with the formation of dialkyldichlorotin.

Similar chemical properties are shown by phosphine oxides of the type: $\left[(C_6H_5)_2\overset{O}{\overset{\|}{P}}-\right]_2SnR_2$.

Boiling water does not react with them, while 15% hydrochloric acid at room temperature splits the tin-phosphorus bond to form diphenylphosphinous acid and dialkyldichlorotin. Caustic potash (20%) forms dialkyltin oxides (identified by means of their chlorides) and diphenylphosphinic acid. Chlorine in chloroform solution cleaves the tin-phosphorus bond at room temperature. As a result of the action of chlorine, dialkyldichlorotin and diphenylphosphinic acid were obtained, because of the saponification of the acid chloride first formed.

Acetyl chloride in boiling benzene solution also cleaved the phosphorus-tin bond. From the products of the reaction with a diphosphine dioxide containing methyl radicals attached to the phosphorus, we isolated dimethyldichlorotin and diphenylphosphinic acid. The course of this reaction requires further investigation.

EXPERIMENTAL

Synthesis of the Esters of Phenylphosphonetrialkyltin

The action of the dimethyl ester of phenylphosphinous acid on trimethyliodotin. In a flask fitted with a reflux condenser and a dropping funnel, there was placed 4.7 g of trimethyliodotin [2], and 2.8 g of the dimethyl ester of phenylphosphinic acid [3] was added drop by drop. The flask was heated on a glycerine bath. At a bath temperature of 80°, a vigorous reaction began, and the temperature inside the flask rose to 240°. Upon cooling, the reaction mixture crystallized. After recrystallization from alcohol, 3.4 g of a colorless finely crystalline substance was obtained with m.p. 132-134°.

0.1320 g substance: 0.1823 g CO_2; 0.0629 g H_2O.
Found %: C 37.66; H 5.30.
$C_{10}H_{17}O_2PSn$. Calculated %: C 37.65; H 5.37.

The action of the diethyl ester of phenylphosphinous acid on trimethyliodotin. To 10.8 g of triethyliodotin, 6.4 g of the diethyl ester of phenylphosphinous acid was added. At a bath temperature of 150°, a quiet reaction began. The temperature of the vapors was 75° (ethyl iodide). Upon cooling, the contents of the flask partly crystallized. The crystals were washed with alcohol and ether. It was impossible to recrystallize them, as the product was insoluble in the usual organic solvents. The product was a colorless finely crystalline powder. Yield 1.6 g, m.p. 294-297°, with decomposition (copper block).

0.1117 g substance: 0.1935 g CO_2; 0.0615 g H_2O.
Found %: C 44.82; H 6.12.
$C_{14}H_{25}O_2PSn$. Calculated %: C 44.83; H 6.73.

The action of the diethyl ether of phenylphosphinous acid on tri-n-butyliodotin. To 9.5 g of tri-n-butyliodotin [4], 4.3 g of the ethyl ester of phenylphosphinous acid was added. At a bath temperature of 185°, the reaction began with the formation of ethyl iodide. Upon cooling, the mass in the flask began to crystallize. The ethyl iodide amounted to 2.9 g, or 86% of theory. There was obtained 1.7 g of a colorless substance with m.p. 302-305°, with decomposition (block). Yield 7.2% of theory.

0.1245 g substance: 0.2378 g CO_2; 0.0862 g H_2O.
Found %: C 52.10; H 7.69.
$C_{20}H_{37}O_2PSn$. Calculated %: C 52.31; H 8.13.

The Reactions of Esters of Phenylphosphonetrialkyltin

1. The action of water. 0.3 g of the methyl ester of phenylphosphonetrimethyl tin was boiled a half hour with water. After removal of the water, the melting point of the ester was unchanged.

2. The methyl ester of phenylphosphonetrimethyltin (0.3 g) was dissolved at room temperature in 10 ml of 15% hydrochloric acid. The solution was extracted several times with ether. After removal of the ether by distillation, 0.11 g of trimethylchlorotin with m.p. 39-41° was obtained from the residue. (A mixed test with trimethylchlorotin gave an unchanged m.p.).

3. The action of 10% caustic potash solution. The methyl ester of phenylphosphonetrimethyltin was dissolved at room temperature in a 10% solution of caustic potash. After standing for three hours, the solution was extracted several times with benzene. After removal of the benzene, the residue was sublimed. There was obtained 0.2 g of the hydrate of trimethyltin oxide, with m.p. 117-120°.

The Synthesis of Esters of Di-(phenylphosphone)-dialkyltin

The action of the dimethyl ester of phenylphosphinous acid on dimethyldiiodotin. To 6 g of dimethyldiiodotin molten in a flask with a reflux condenser, 5.1 g of the dimethyl ester of phenylphosphinous acid was added drop by drop.

After a few minutes, a vigorous reaction began. The temperature in the flask reached 180°. After cooling, the contents of the flask began to crystallize. The methyl iodide was removed under vacuum. The crystalline substance was filtered off, and washed with water and alcohol. There was obtained 3.7 g of a crystalline substance with m.p. 291-293°, with decomposition (block), or 54.5% of theory.

0.2101 g substance: 0.3241 g CO_2; 0.0931 g H_2O.
Found %: C 42.07, H 4.92.
$C_{18}H_{22}O_4P_2Sn$. Calculated %: C 41.85; H 4.84.

The action of the diethyl ester of phenylphosphinous acid on diethyldiiodotin. To the melted diethyldiiodotin (7.0 g), placed in a flask with a reflux condenser, was added 6.5 g of the diethyl ester of phenylphosphinous acid; the mixture was heated on the oil bath. At a bath temperature of 150°, a reaction began, with the separation of ethyl iodide (the temperature of the vapors was 73°). The temperature in the flask rose to 190°, and then began slowly to fall; the contents of the flask began to crystallize. The crystals were removed, and washed with alcohol and ether. They weighed 2.8 g. They could not be recrystallized because of their insolubility. The crystals had a weak yellow color. M.p. 296-300°, with decomposition (block). Yield, 33.5% of theory.

0.1050 g substance: 0.1782 g CO_2; 0.0535 g H_2O.
Found %: C 46.28; H 5.66.
$C_{20}H_{30}O_4P_2Sn$. Calculated %: C 46.62; H 5.89.

The action of the di-n-propyl ester of phenylphosphinous acid on diethyldiiodo tin. To 4.5 g of melted diethyldiiodotin, 5.0 g of the di-n-propyl ester of phenylphosphinous acid was added. The reaction began at a bath temperature of 195°. At the end of the reaction, the contents of the flask began to crystallize. The propyl iodide was distilled off under vacuum (loss in weight 3.4 g, or 90% of theory). The crystalline material was separated, and washed with alcohol and ether; it was in the form of fine colorless crystals with m.p. 245-248°, with decomposition (block). Yield 61.4% of theory. It was impossible to purify the substance by recrystallization. The substance burned only with difficulty.

0.1218 g substance: 0.1921 g CO_2; 0.0516 g H_2O.
Found %: C 42.02; H 5.13.
$C_{22}H_{34}O_4P_2Sn$. Calculated %: C 48.62; H 6.32.

A Study of the Reactions of the Esters of Di-(phenylphosphone)-dialkyltin

1. The action of water. The methyl ester of di-(phenylphosphone)-dimethyltin (0.3 g) was boiled for 3 hours with water. After filtration and drying, the melting point was unchanged.

2. The action of hydrochloric acid. 0.4 g of the methyl ester of di-(phenylphosphone)-dimethyltin was dissolved at room temperature in 15 ml of 15% hydrochloric acid. After several extractions with ether and evaporation of the ether, the solution gave 0.12 g of dimethyldichlorotin with m.p. 101-105°. A mixed test with dimethyldichlorotin gave m.p. 103-105°.

3. The action of alkali. 1 g of the methyl esters was dissolved in 25 ml of a 10% solution of caustic soda. After boiling for three hours with a reflux condenser, the alcohol and part of the water were removed by distillation under vacuum.

After these were removed, a white amorphous precipipitate formed; this was separated and washed with water. This substance was diethyltin oxide, as was shown by the fact that treatment with hydrobromic acid transformed it quantitatively into diethyldibromotin, with m.p. 62°. A mixed test with diethyldibromotin gave no lowering of the m.p.

4. The action of chlorine. To 1 g of the ethyl ester of di-(phenylphosphone)-diethyltin, the calculated quantity of chlorine was added in a chloroform solution. After 20 minutes, the ester went into solution, and the solution was decolorized. After removal of the chloroform by distillation, the precipitate was sublimed to give 0.41 g of diethyldichlorotin, with m.p. 84°.

Synthesis of the Oxides of Diphenyltrialkylstannylphosphines

The ethyl ester of diphenylphosphinous acid. The ester was obtained by the action of ethyl alcohol on diphenylphosphorochloride in the presence of dimethylaniline, and had b.p. 161-163° at 10 mm [5]. Yield, 51% of theory.

The methyl ester, obtained similarly, had b.p. 152-155° at 10 mm. Yield 53%.

The diphenylphosphorochloride needed for the synthesis was obtained by heating phosphenyl chloride in sealed tubes up to 300°. It appeared unnecessary to heat the tubes for 96 to 120 hours, as Doerken recommended. The same yields of diphenylphosphorochloride (36%) were obtained after 8 hours of heating.

The action of the ethyl ester of diphenylphosphinous acid on triethyliodotin. Triethyliodotin (7 g) was placed in a flask with a reflux condenser, and 4.9 g of the ethyl ester of diphenylphosphinous acid was added. The reaction began at 170°. The ethyl iodide was removed after the reaction in vacuum. Upon cooling, the contents of the flask crystallized. The crystals were removed, and washed with alcohol and ether. There was obtained 0.43 g, or 5.1% of theory. M.p. 346-348°, with decomposition (block). After standing for two days, additional crystals separated from the filtrate; after recrystallization from alcohol, these had m.p. 121-124°, and appeared to be the oxide of diphenylethylphosphine. A mixed test with the oxide of diphenylethylphosphine gave no depression [5]. Yield 1.4 g. Below is the analysis of the material with m.p. 346-348°.

0.0615 g substance: 0.1242 g CO_2; 0.0301 g H_2O.
Found %: C 55.07; H 5.44.
$C_{18}H_{25}OPSn$. Calculated %: C 53.08; H 6.19.

It was impossible to purify the substance by recrystallization.

The action of the ethyl ester of diphenylphosphinous acid on trimethyliodotin. To 5.1 g of trimethyliodotin, 4 g of the ethyl ester of diphenylphosphinous acid was added. Upon heating to a bath temperature of 195°, the reaction began, with the separation of ethyl iodide. After cooling, a thick viscous mass was obtained. It was dissolved in alcohol. From the alcoholic solution, there separated out crystals which, after removal and washing with alcohol and ether, had m.p. 365-368° with decomposition (block). Yield 0.65 g, or 9.8% of theory. From the filtrate, 1.7 g of the oxide of diphenylethylphosphine was separated; this had m.p. 118-122°.

0.0391 g substance: 0.0743 g CO_2; 0.0165 g H_2O.
Found %: C 51.82; H 4.69.
$C_{15}H_{19}OPSn$. Calculated %: C 49.32; H 5.27.

The action of the methyl ester of diphenylphosphinous acid on triethyliodotin. In order to decrease the isomerization of the ester of diphenylphosphinous acid under the influence of the methyl iodide which separated out during the reaction,

the synthesis was carried out with an ordinary condenser.

To 4.6 g of the triethyliodotin, placed in a flask with a direct condenser, 3 g of the methyl ester of diphenylphosphinous acid was added through a dropping funnel. No reaction was observed. Upon heating the reaction to 190°, a vigorous momentary reaction ensued. The temperature in the flask rose to 250°. Upon distillation of the contents of the flask in vacuum, triethyliodotin (b.p. 111-112° at 10 mm) came over to the amount of 4.2 g or 91.5% of the amount used in the reaction. The residue in the flask crystallized, and appeared to be the oxide of diphenylmethylphosphine with m.p. 108-110° [5].

The Synthesis of Phosphine Oxides of the Type $\left[(C_6H_5)_2\overset{\overset{O}{\|}}{P}\right]_2SnR_2$

The action of the ethyl ester of diphenylphosphinous acid upon dimethyldiiodotin. To 6.0 g of molten dimethyldiiodotin, placed in a flask fitted with a reflux condenser, 6.9 g of the ethyl ester of diphenylphosphinous acid was added. The reaction began at an oil bath temperature of 140°, and the temperature inside the liquid rose to 230°, the temperature of the vapors to 73°. The contents of the flask began to crystallize even before cooling. The crystals were washed with alcohol and ether. There was obtained 2.2 g of a colorless, crystalline substance with m.p. 372-375° with decomposition (block). Yield 26.6% of theory. Because of the insolubility of the crystals in organic solvents, it was impossible to recrystallize them.

0.0317 g substance: 0.0653 g CO_2; 0.0132 g H_2O.
Found %: C 56.16; H 4.63.
$C_{28}H_{28}O_2P_2Sn$. Calculated %: C 56.63; H 4.76.

After washing with alcohol and ether, 0.9 g of the oxide of diphenylethylphosphine was obtained from the filtrate:, m.p. 119-122°.

The action of the ethyl ester of diphenylphosphinous acid on diethyldiiodotin. 5.6 g of diethyldiiodotin and 6 g of the ethyl ester of diphenylphosphinous acid were heated in a small flask with a reflux condenser on an oil bath. At 115°, the reaction began, with the separation of ethyl iodide. The temperature in the flask rose to 190° and the contents crystallized. The ethyl iodide was distilled off in vacuum. The weight of the flask decreased by 2.6 g, which corresponded to 64% of the theoretically calculated quantity of ethyl iodide. The crystals were washed with alcohol and ether. They were obtained to the amount of 1.3 g or 17.3% of theory. M.p. 351-353°. Because of their lack of solubility, they could not be recrystallized.

0.0743 g substance: 0.1580 g CO_2; 0.0360 g H_2O.
Found %: C 57.99; H 5.38.
$C_{28}H_{30}O_2P_2Sn$. Calculated %: C 58.06; H 5.22.

Diphenylethylphosphine oxide was isolated from the filtrate.

Investigation of the Reactions of Phosphine Oxides of the Type $\left[(C_6H_5)_2\overset{\overset{O}{\|}}{P}\right]_2SnR_2$

1. The action of water on $[(C_6H_5)_2P(O)]_2Sn(CH_3)_2$. 0.3 g of the substance was boiled for 3 hours with water. The substance was recovered unchanged.

2. The action of hydrochloric acid (15%) on the diethyl derivative. 0.2 g of the substance was boiled in 15 ml of 15% hydrochloric acid until it dissolved. The formation of crystals of some other form was observed. After the crystals had been separated and washed with ether they had m.p. 193-194°. A mixed test with diphenylphosphinous acid showed no change in melting point. The hydrochloric acid filtrate was extracted with ether and the ether removed; there remained crystals of

diethyldichlorotin, with m.p. 78-81°.

3. The action of alkali. The dimethyl derivative (0.5 g) was dissolved at room temperature in 15 ml of a 20% solution of caustic potash. Upon boiling this solution for 40 minutes, an oil floated to the surface; it crystallized upon cooling. M.p. 69-74°. Upon acidification of the aqueous solution of this substance with hydrochloric acid, needle-shaped crystals separated out with m.p. 192-194°. A mixed test with diphenylphosphinic acid gave no m.p. depression. The alkaline solution, obtained after removal of the sodium diphenylphosphinate, was strongly acidified with hydrochloric acid, and the solution extracted with ether. After the ether had been evaporated off dimethyldichlorotin was obtained, with m.p. 98-104°.

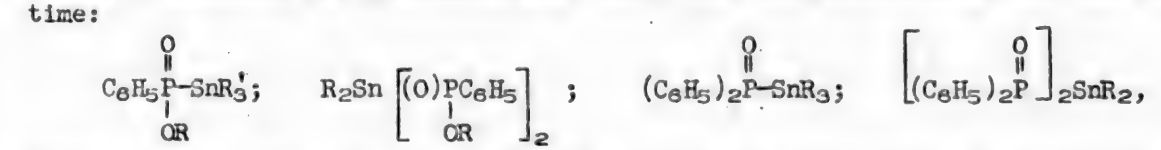
4. The action of chlorine. To 0.23 g of the dimethyl derivative at room temperature, a solution of 0.06 g of chlorine in chloroform was added, and the solution allowed to stand for 6 hours. The crystals of the dimethyl derivative went completely into the solution, and decolonized it. The chloroform was driven off, and the crystalline residue was extracted with ether. Dimethyldichlorotin was recovered from the ether solution with m.p. 105-107°. The residue insoluble in ether was recrystallized from alcohol; it then had m.p. 191-193°. Mixed test with diphenylphosphinic acid showed no depression.

5. The action of acetyl chloride. To 0.5 g of the dimethyl derivative a solution of 0.15 g of acetyl chloride in 15 ml of dry benzene was added. The mixture was boiled for an hour with a reflux condenser. The crystals went into solution. After removal of the benzene the residue solidified to give two kinds of crystals: needles and warts. The needle-shaped crystals were separated by solution in ether and appeared to be dimethyldichlorotin, with m.p. 107° (mixed test). The wart-shaped crystals were recrystallized from alcohol and had m.p. 193-195°. A mixed test with diphenylphosphinic acid gave no depression.

SUMMARY

1. The action of alkylhalogen tin derivatives on the esters of phenylphosphinous and diphenylphosphinous acid has led to the synthesis of phosphorus-tin compounds containing phenyl radicals attached to the phosphorus.

2. Representatives of the following types of organic derivatives of phosphorus, containing the phosphorus-tin bond, have been synthesized for the first time:



where R and R' are alkyl radicals. In all, 10 new phosphorus-tin compounds have been described.

3. It has been shown that in the compounds obtained, the phosphorus-tin bond is easily broken by the action of hydrochloric acid, caustic potash, and chlorine. The phosphorus-tin bond is not broken by boiling with pure water.

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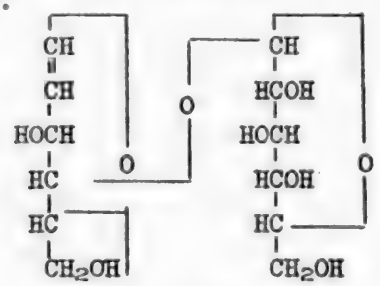
THE DETERMINATION OF THE STRUCTURE OF DISACCHARIDES

II. DETERMINATION OF THE STRUCTURE OF MALTOSE

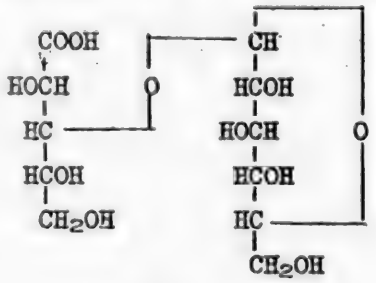
A. M. Gakhokidze

In our previous work [1] we determined the structure of glucosido-3-glucose. In the present paper, we are giving a determination of the structure of maltose.

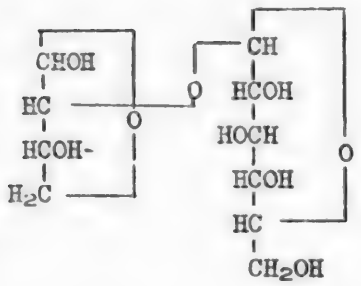
Maltose was converted by the usual method, through the octaacetate [2], acetobromomaltose [3], and hexaacetylmaltal [4] into maltal (I). Upon oxidation of the maltal with potassium permanganate, glucosido-3-arabonic acid (II) was obtained; the calcium salt of this acid was converted, by oxidative cleavage with perhydrol, into glucosido-2-erythrose (III). Glucosido-2-erythrose gives no osazone with phenylhydrazine. Upon hydrolysis of methylated glucosido-2-erythronic acid (IV), dimethylerythronic acid (V) was obtained; oxidation of the latter gave dimethylglycerinic acid (VI). Thus, the second carbon atom of erythrose takes part in the formation of the biose bond, and maltose has the structure (1,5)-glucosido-4-(1,5)-glucose.



(I)



(II)



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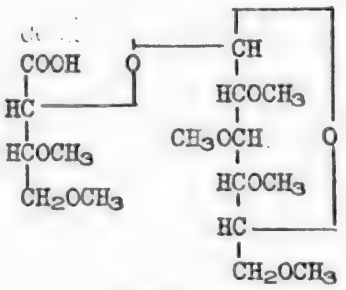

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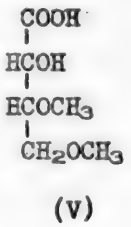

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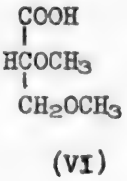

(VI)

EXPERIMENTAL

1. The Oxidation of Maltal

84.5 g of maltal was dissolved in 400 ml of water, and to this solution 150 ml of a 5% potash solution was added; this was strongly shaken, and gentle heating (30-50°) was applied while a 4% solution of potassium permanganate was gradually

added. The addition of the permanganate solution was continued until the drops of solution were no longer decolorized.

The filtered solution was evaporated under reduced pressure to dryness. The residue was dissolved in 200 ml of water, and from the solution obtained, glucosido-arabonic acid was precipitated with basic lead acetate. The precipitate was filtered off, washed, and suspended in water, from which the lead was precipitated out by hydrogen sulfide. After removal of the lead sulfide, the filtrate was boiled for 15 minutes to remove the excess of hydrogen sulfide.

The solution was neutralized with calcium carbonate, filtered, and concentrated to a minimal volume. Upon the addition to the concentrated solution of absolute ethyl alcohol, amorphous flocs of the calcium salt of glucosido-3-arabonic acid precipitated out. The salt was purified by two recrystallizations from hot water. Yield 4.2 g, i.e., 60% of theory.

0.1321 g substance: 0.0115 g CaO.
0.1762 g substance: 0.0149 g CaO.
Found %: Ca 6.22, 5.98.
$(C_{11}H_{19}O_{11})_2Ca$. Calculated %: Ca 5.77

2. Oxidation of the Calcium Salt of Glucosido-3-arabonic Acid

In a round-bottomed liter flask, 63.6 g of the calcium salt of glucosido-3-arabonic acid was dissolved in 700 ml of water. To this solution, 5.6 g of barium acetate in 60 ml of water and 3.2 g of ferric sulfate were added. The solution was boiled for 10 minutes and then filtered. To the cooled solution, 80 ml of a 30% perhydrol solution was added with vigorous stirring. After 3 hours, an additional 20 ml of perhydrol solution was added to the reaction mixture. The solution was warmed gently on the water bath, and filtered through bone charcoal on a Buchner funnel. It was then evaporated under reduced pressure to a minimal volume and mixed with absolute methyl alcohol. After several days, crystals separated out; these were recrystallized from hot water. Yield, 20.1 g, i.e., 79% of theory. The melting point of the pure glucosido-2-erythrose was 141°; $(\alpha)_D^{20}$ + 87.5 (in water).

0.1269 g substance: 0.1650 g CO_2; 0.0801 g H_2O.
0.1994 g substance: 0.2101 g CO_2; 0.1226 g H_2O.
Found %: C 41.95, 42.39; H 6.95, 6.67.
$C_{10}H_{18}O_9$. Calculated %: C 42.61; H 6.38.

Upon the acetylation of glucosido-2-erythrose with acetic anhydride in the presence of sodium acetate, hexaacetylglucosido-2-erythrose was obtained, with m.p. 127°.

0.1601 g substance: 18.1 ml 0.1 N NaOH.
0.1667 g substance: 18.6 ml 0.1 N NaOH.
Found %: $COCH_3$ 48.82, 48.29.
$C_{22}H_{30}O_{15}$. Calculated %: $COCH_3$ 48.30.

3. The Oxidation of Glucosido-2-erythrose and the Cleavage of the Acid Obtained

19.2 g of glucosido-2-erythrose was dissolved in 300 ml of bromine water, and the solution frequently shaken while being allowed to stand in the light for 3 days. After neutralization with calcium carbonate, the solution was filtered and the excess of bromine removed by boiling for 10 minutes. Upon the addition of absolute ethyl alcohol to the strongly concentrated solution, flocs of the calcium salt of glucosido-2-erythronic acid precipitated out. Yield 15.6 g, i.e., 77% of theory.

0.1022 g substance: 0.0096 g CaO.
0.1295 g substance: 0.0128 g CaO.
Found %: Ca 6.71, 7.01.
$(C_{10}H_{17}O_{10})_2Ca$ Calculated %: Ca 6.31.

15.1 g of the calcium salt of glucosido-2-erythronic acid was dissolved in 250 ml of water, and the calcium precipitated from this solution with the calculated quantity of oxalic acid. The solution, after filtering off the calcium oxalate, was heated to boiling with 100 ml of 5% sulfuric acid solution for 20 minutes. The solution was then neutralized with calcium carbonate, filtered, and concentrated to a minimal volume. Upon the addition of absolute ethyl alcohol to the concentrated solution, flocs of the calcium salt of d-erythronic acid were precipitated.

0.1283 g substance: 0.0226 g CaO.
Found %: Ca 12.81.
$(C_4H_7O_5)_2Ca$. Calculated %: Ca 12.90.

Upon decomposing the calcium salt of d-erythronic acid with the calculated amount of oxalic acid, and then concentrating the filtered solution, the γ-lactone of erythronic acid was obtained, with m.p. 101-102°, $[\alpha]_D^{20}$ − 78.3° (in water).

The phenylhydrazide of d-erythronic acid has m.p. 128-130°, which agrees with the data of the literature [5].

0.1207 g substance: 13.3 ml N_2 (16°, 732 mm).
0.1364 g substance: 15.6 ml N_2 (16°, 732 mm).
Found %: N 12.83, 13.19.
$C_{10}H_{14}N_2O_4$. Calculated %: N 12.28.

After the removal of the calcium salt of d-erythronic acid, the solution was treated with phenylhydrazine; it gave an osazone with m.p. 207°. A mixed test with glucosazone, obtained from pure glucose, showed no depression.

4. The Oxidation of Dimethylerythronic Acid

4.6 g of the calcium salt of dimethyl-d-erythronic acid was dissolved in 50 ml of water. To this solution was added 2 g of barium acetate and 1.2 g of ferric sulfate, dissolved in 40 ml of water. The reaction mixture was filtered and heated gently while 25 ml of 30% perhydrol was added. The mixture was allowed to stand for 24 hours. Then the solution was boiled for 10 to 15 minutes, filtered, mixed with 100 ml of bromine water, and allowed to stand in the light for 3 days. In order to remove the excess of bromine, the solution was boiled for 10 to 15 minutes, and then heated with calcium carbonate. The solution was filtered from the excess of calcium carbonate and evaporated to a small volume. Upon gradual addition to the concentrated solution of absolute ethyl alcohol, flocs of the calcium salt of dimethylglyceric acid were precipitated.

0.1718 g substance: 0.0325 g CaO.
Found %: Ca 13.52.
$(C_5H_9O_4)_2Ca$. Calculated %: Ca 13.07.

Methylation of the calcium salt of dimethylglyceric acid with dimethyl sulfate in the presence of alkali gave the methyl ester of dimethylglyceric acid, with b.p. 78-89° (at 15-16 mm), d_4^{20} 1.0598, n_D^{20} 1.4584.

0.1348 g substance: 0.6430 g AgI.
Found %: OCH_3 62.57.
$C_8H_{12}O_4$. Calculated %: OCH_3 62.83.

SUMMARY

1. The oxidation of maltal with potassium permanganate gave glucosido-2-arabonic acid.

2. The oxidation of the calcium salt of glucosido-2-arabonic acid with perhydrol gave glucosido-2-erythrose.

3. Glucosido-2-erythronic acid was obtained.

4. The oxidation of 3,4-dimethylerythronic acid gave 2,3-dimethylglyceric acid.

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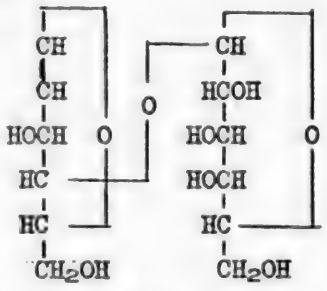
*See CB translation p. a571 ff.

THE DETERMINATION OF THE STRUCTURE OF DISACCHARIDES

III. DETERMINATION OF THE STRUCTURE OF LACTOSE

A. M. Gakhokidze

Lactose was converted into the octaacetate, then into acetobromolactose and hexaacetyllactyl [1]; the latter was converted into lactal (I). The oxidation of lactal with potassium permanganate in the presence of potash gave galactosido--3-arabonic acid (II). Oxidation of the calcium salt of galactosido-3-arabonic acid with perhydrol gave galactosido-2-erythrose (III), which was easily reduced with Fehling's solution, but did not give an osazone. From these considerations, it was determined that the 2nd carbon atom of erythrose (i.e., the 4th carbon atom of the original glucose in the disaccharide) takes part in the formation of the biose bond.



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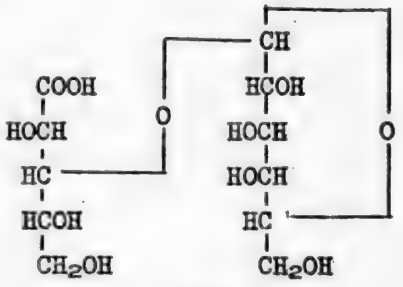

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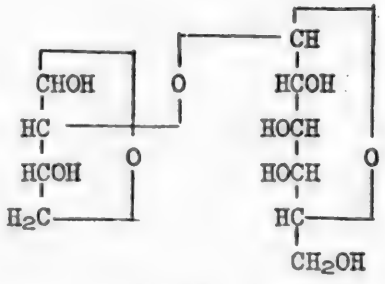

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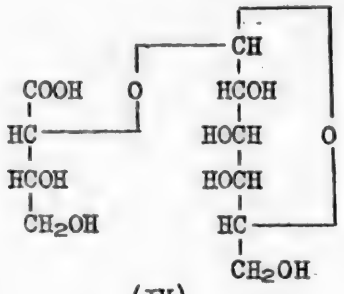

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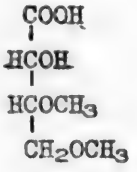

(V)

A further indication of the position of the oxygen bridge was the oxidation of galactosido-2-erythrose to give galactosido-2-erythronic acid (IV), with subsequent oxidation of the dimethylerythronic acid (V), obtained by hydrolysis of the methylated galactosido-2-erythronic acid, to dimethylglyceric acid.

It was thus determined that the fourth carbon atom of the reducing portion of the disaccharide takes part in the formation of the biose bond.

1. The Oxidation of Lactal

76.8 g of lactal (with m.p. 190-191°; $[\alpha]_D^{20} = +25.7°$, in water) was dissolved in 500 ml of water; 200 ml of a 5% potash solution was added to this solution,

and then, with vigorous shaking, a 4% solution of potassium permanganate was gradually added. The addition of the permanganate solution was continued until the reaction mixture had a weak rose color. The solution was filtered, and evaporated to dryness under reduced pressure. The residue was dissolved in 300 ml of water, and galactosido-3-arabonic acid was precipitated from this solution by means of basic lead acetate. The precipitate was filtered off, washed, and suspended in water; the lead was precipitated from this suspension with hydrogen sulfide. After removal of the lead sulfide, the filtrate was boiled for 15 minutes to remove the excess of hydrogen sulfide. The solution was then boiled with calcium carbonate. The filtered solution was concentrated in vacuum to a minimal volume. Upon gradual addition to this solution of absolute ethyl alcohol, amorphous flocs of the calcium salt of galactosido-3-arabonic acid precipitated. Yield 44.2 g, i.e., 45% of theory. The salt was purified by recrystallization from hot water.

0.1417 g substance: 0.0115 g CaO.
0.1778 g substance: 0.0153 g CaO.
Found %: Ca 5.82, 6.17.
$(C_{11}H_{19}O_{11})_2Ca$. Calculated %: Ca 5.77.

2. The Oxidation of the Calcium Salt of Galactosido-3-arabonic Acid

In a 1½ liter round-bottomed flask, 43.5 g of the calcium salt of galactosido-3-arabonic acid was dissolved in 800 ml of water and to this solution were added 5.3 g of barium acetate in 50 ml of water and 4.4 g of ferric sulfate. After 15 minutes of boiling, the solution was filtered. To the cooled solution, 80 ml of 30% perhydrol solution was added. The temperature of the reaction medium was not allowed to rise above room temperature. After 3 hours, an additional 35 ml of perhydrol was added to the reaction solution. At the end, the solution was gently heated on the water bath. It was then filtered through wood charcoal on a Buchner funnel and evaporated to a minimum volume under reduced pressure. Upon gradual addition of absolute methyl alcohol to the concentrated solution, crystals precipitated out. The β-galactosido-2-erythrose obtained was recrystallized twice from hot water. Yield 21.4 g, i.e., 60% of theory. M.p. of the pure compound 154-155°; $[\alpha]_D^{20}$ = +22.5° (in water).

Zemplen [2] describes galactosido-2-erythrose as a syrup with $[\alpha]_D^{20}$ = +18° (in water).

0.1222 g substance: 0.1881 g CO_2; 0.0763 g H_2O.
Found %: C 42.19; H 7.02.
$C_{10}H_{18}O_9$. Calculated %: C 42.58; H 6.32.

The acetylated galactosido-2-erythrose has m.p. 138-140°.

0.3667 g substance: 41.6 ml 0.1 N NaOH
0.3030 g substance: 33.4 ml 0.1 N NaOH
Found %: $COCH_3$ 48.49, 48.27.
$C_{22}H_{30}O_{15}$. Calculated %: $COCH_3$ 48.30.

3. The Oxidation of Galactosido-2-erythrose and the Cleavage of the Acid Obtained

19.8 g of galactosido-2-erythrose was dissolved in 400 ml of bromine water, and this solution was allowed to stand in the light, with frequent shaking. In case the solution was decolorized, a few additional millilitres of bromine water were added. After 4 days, the solution was heated to boiling and neutralized with calcium carbonate. The solution was filtered off from the excess of calcium carbonate and evaporated to a minimal volume. Upon the gradual addition of absolute ethyl alcohol to the concentrated solution, a precipitate of the calcium salt of galactosido-2-erythronic acid was formed. This was filtered off and dried. Yield, 15.9 g,

i.e., 64% of theory.

0.1679 g substance: 0.0142 g CaO.
Found %: Ca 6.02.
$(C_{10}H_{17}O_{10})_2Ca$. Calculated %: Ca 6.45.

3.7 g of the calcium salt of galactosido-2-erythronic acid was dissolved in 150 ml of water and the calcium removed from this solution with a calculated quantity of oxalic acid. After removal of the calcium oxalate, the filtrate was boiled with 100 ml of a 5% solution of sulfuric acid. Then the solution was neutralized with calcium carbonate, filtered, and concentrated to a small volume.

Upon the gradual addition to the concentrated solution of absolute alcohol flocs of the calcium salt of erythronic acid were precipitated. The precipitate was filtered off and dried.

0.1162 g substance: 0.0218 g CaO.
0.1448 g substance: 0.0265 g CaO.
Found %: Ca 13.49, 12.04.
$(C_4H_7O_5)_2Ca$. Calculated %: Ca 12.90.

The precipitate of calcium salt (after analysis of the calcium) was dissolved in 100 ml of water and the calcium precipitated from this solution with the calculated amount of oxalic acid. Upon evaporation of the filtered solution to dryness in vacuum, there was obtained the γ-lactone of d-erythronic acid, with m.p. 103-104° $[\alpha]_D^{20} = -69.9°$ (in water). According to the literature [3], the lactone of d-erythronic acid has m.p. 103°, $[\alpha]_D^{20} = -73.3°$ (in water). The phenylhydrazide of d-erythronic acid melted at 128-131°. According to the literature [4], the phenylhydrazide of d-erythronic acid has m.p. 128°.

0.1074 g substance: 12.6 ml N_2 (13°, 732 mm).
0.1281 g substance: 15.1 ml N_2 (13°, 732 mm).
Found %: N 13.60, 13.49.
$C_{10}H_{14}N_2O_4$. Calculated %: N 12.28.

After removal of the calcium salt of erythronic acid, the solution was heated with acetic acid and phenylhydrazine. The yellow precipitate obtained was filtered off and recrystallized from alcohol. The melting point of the pure substance was 195-197°. A mixed test with galactosazone gave no depression.

10.6 g of the calcium salt of galactosido-2-erythronic acid was dissolved in 100 ml of water. This solution was heated to 60-70°, and 100 ml of dimethyl sulfate added; then there was gradually added, with vigorous stirring, a 25% solution of caustic soda at such a rate that the reaction medium was at all times maintained weakly alkaline.

At the end of the reaction, the solution was boiled for 10 to 15 minutes. The methylated product was extracted from the solution with chloroform. After drying, and evaporation of the chloroform, there was obtained a syrup of the methyl ester of hexamethylgalactosido-2-erythronic acid with n_D^{20} 1.5074. Yield 9.9 g, or 71% of theory.

0.1013 g substance: 0.4059 g AgI.
Found %: OCH_3 54.47.
$C_{17}H_{32}O_{10}$. Calculated %: OCH_3 54.89.

9.7 g of the methyl ester of hexamethylgalactosido-2-erythronic acid was heated at the boiling point for 20 minutes with 250 ml of a 5% solution of sulfuric acid. The solution was then neutralized with calcium carbonate and filtered. Upon the gradual addition of absolute ethyl alcohol to the concentrated solution, flocs of the calcium salt of dimethyl-d-erythronic acid precipitated out.

The calcium salt obtained was dissolved in 150 ml of water, and 2.8 g of barium acetate and 1.5 g of ferric sulfate dissolved in 30 ml of water were added.

The reaction mixture was heated for a short time, and then cooled; 50 ml of a 30% solution of perhydrol was added. After 3 hours, an additional 10 ml of perhydrol was added.

The solution was filtered and mixed with 100 ml of bromine water, and then allowed to stand in the light for 3 days with frequent shaking. After neutralization with $CaCO_3$, the solution was filtered and concentrated to a minimal volume. Upon the addition of absolute ethyl alcohol to the concentrated solution, flocs of the calcium salt of dimethylglyceric acid precipitated out.

0.2009 g substance: 0.0362 g CaO.
Found %: Ca 12.86.
$(C_5H_9O_4)_2Ca$. Calculated %: Ca 13.07.

Upon methylation of the Ca salt of dimethylglyceric acid with dimethyl sulfate in the presence of alkali, the methyl ester of dimethylglyceric acid was obtained; it had b.p. 78-80° (at 13 mm); d_4^{20} 1.0613; n_D^{20} 1.4610.

0.1012 g substance; 0.4772 g AgI.
Found %: OCH_3 62.98.
$C_8H_{12}O_8$. Calculated %: OCH_3 62.83.

SUMMARY

1. The oxidation of lactal by means of potassium permanganate gave galactosido-3-arabonic acid.

2. The oxidation of galactosido-3-arabonic acid with perhydrol gave galactosido-2-erythrose.

3. Galactosido-2-erythronic acid has been obtained.

4. The methyl ester of heptamethylgalactosido-2-erythronic acid has been obtained.

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SULFONATION OF SALTS OF SULFUROUS ACID

XIV. THE MECHANISM OF "OXIDATIVE" SULFONATION

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We consider "oxidative" sulfonation to be the formation of sulfo-acids, produced by the action on any compound of sulfurous acid or salts and oxidizing agents derived from the latter. Hence we exclude those cases where sulfonation is accompanied by the reduction of substituents in the same molecule of the sulfonated compound, as in the case of quinones, and nitro and nitroso compounds, as well as sulfonation in the presence of such extraneous oxidizing agents as aromatic o- and p-dihydroxy, aminohydroxy, and diamino compounds. With the first group, and possibly with the second as well, the mechanism of sulfonation must be distinguished from "oxidative" sulfonation proper.

Oxidative sulfonation with sulfurous acid and manganese dioxide was first observed by H. Leuchs and coworkers (1908-1912), with strychnine and brucine; later, J. Garreau (1934), by the action of oxygen with ammonium sulfite and copper oxide in ammoniacal solution on phenol and guaiacol obtained the sulfonic acids of phenol and guaiacol.

We have shown [1] that the oxidation of an aqueous solution of sodium sulfite in the presence of 2-naphthol, 2-hydroxy-3-naphthoic acid 2,4-, 2,6-, and 2,7-naphtholsulfonic acids, and 2-naphthol-3,6-disulfonic acid also leads to the sulfonation of the hydroxy compound, with substitution taking place in position 1. A number of oxidizing agents lead to the formation of sulfonic acids: MnO_2, PbO_2, HgO, CuO, Fe_2O_3, air, nitric oxide, sodium nitrite, aromatic nitro and nitroso compounds. Here we may also refer to P. Baumgarten's [2] observation of the formation of anhydro-N-pyridinium sulfonic acid by the oxidation of a mixture of sulfite and pyridine with copper sulfate, monopersulfuric acid, or air, and the formation of aminosulfonic acids by the oxidation of sulfite with potassium persulfate, monopersulfuric acid, or the action of an anode, all in the presence of ammonia.

H. Leuchs and W. Schneider considered that the formation of sulfonic acid was the result of a process similar to the one leading to the formation of dithionates:

$$R - H + O + H - SO_3H = R - SO_3H + H_2O$$

($R = SO_3H$ or the rest of the organic molecule).

According to P. Baumgarten and H. Erbe, monopersulfuric acid and the salts of bivalent Cu change the SO_3'' ion into the $(SO_2 - O -)'$ ion, and the other oxidizing agents form the $(-SO_3)'$ ion; both products of oxidation result in the sulfonation of ammonia, as for example:

$$NH_3 + (-SO_3)' \longrightarrow NH_3, - SO_3' \xrightarrow{+(-SO_3)'} NH_2 - SO_3H + SO_3''.$$

Anhydro-N-pyridinium sulfonic acid is obtained similarly, but only by way of the $(SO_2-O-)'$ ions. V.A. Izmailsky [3] explained our case of the sulfonation of hydroxy compounds by means of the formation of sulfinic acids and their oxidation. In our experiments with MnO_2, HgO, $NaNO_2$, nitro and nitroso compounds, and diazosulfonate, it was shown that sulfonation takes place because of oxidation of the sulfite in such a way as to change it into sulfate (the last five oxidizing agents, in the absence

of the sulfonation process, can give only sulfate). We further determined the sulfonating tendency of individual derivatives of sulfurous acid, like

(I) $[Hg(SO_3)_2]Na_2$; (II) $HON(SO_3K)_2$; (III) K_2SO_3, 2NO;

(I) sulfonates 2-hydroxy-3-naphthoic acid, 1-naphthol, aniline, and 1-naphthylamine: the amino compounds are substituted both in the aminogroup and in the nucleus. (II) and (III) sulfonate aniline, the substituent entering exclusively or almost exclusively into the amino group: they do not sulfonate hydroxy compounds. Upon reaction with water, these compounds give sulfate. The dependence of the direction of substitution on the structure of the organic substance and on the composition of the sulfonating compound shows that sulfonation and the formation of sulfate do not take place by way of a preliminary cleavage of the sulfonating compound, but by way of its interaction with the organic compound or with water.

To complete this series of investigations it was of interest to trace the course of the oxidation of sulfite with other oxidants – both those which lead to sulfate, as well as those which form large amounts of dithionate. To the first group belong iodine, hydrogen peroxide, potassium persulfate and permanganate, and quinone. According to H. Bassett and A. Henry [4], iodine, hydrogen peroxide, and permanganate oxidize neutral sulfite only to sulfate; the oxidation of sulfurous acid and acid salts can give dithionate with a yield up to 0.8, 1.0, and 24% of the SO_2 oxidized. During the oxidation of sulfite with persulfate, 2% of the SO_2 oxidized [5], is transformed into dithionate; in the presence of coordination-unsaturated compounds such as pyridine, dioxane, fluoride, and excess of sulfite, and so on, the yield of dithionate sharply increases [2]. The action of quinone on sulfite does not form dithionate [6]. Among the oxidizing agents which lead to the formation of dithionate, we must place silver, copper, and iron compounds. Silver sulfite, on decomposition in water, gives 89.8% of silver dithionate; the oxidation of sulfite with silver nitrate, used in the ratio 3:1, leads to a 97.5% yield of sodium dithionate, basing the calculation on the silver used [7]. The oxidation of sulfite with copper sulfate, at room temperature, with a ratio of $Cu^{\cdot\cdot}:SO_3''$ of 1:3 or 1:4, gives 45-69% or 82% of dithionate, basing the calculation on the copper salt, [8]. Ferric oxide and sulfurous acid give an almost theoretical yield of dithionate; a weakly acid solution of ferric chloride reacts with sulfite to give only 36-46% of dithionate, while in alkaline solution the yield of dithionate is increased, [9].

In our experiments on the oxidation of sulfite, we used an insufficient amount of oxidizing agent; this to some extent permitted us, at a suitable concentration of the organic substance, to keep it from reacting directly with the oxidizing agent.

The oxidation of sulfite with iodine and hydrogen peroxide at 50° in the presence of 2-naphthol-7-sulfonic acid, as well as the oxidation with potassium persulfate in the presence of 2,4- and 2,7-naphtholsulfonic acids at 30-50° and 50-85° did not lead to the formation of sulfonation products; the use of alkaline sulfite solution during the oxidation with iodine did not change these results.

The oxidation of sulfite with permanganate at 70° in the presence of 2-hydroxy-3-naphthoic acid, 2,4-, 2,6-, and 2,7-naphtholsulfonic acids, and 2-naphthol-3,6-disulfonic acid gave products of the sulfonation of the hydroxy compounds, with yields from 14.5 to 28% of the amount of sulfite oxidized. But we may suppose that the chief reason sulfonation took place was not the reduction of the permanganate, but the further reduction of the manganese dioxide. A sum of the quantities of sulfite used up to form sulfate and sulfonic acid is close to the amount of sulfite transformed into sulfate in the absence of the compound which is sulfonated.

In the reaction of 1,2-naphthoquinone-4-sulfonic acid with bisulfite in the presence of 2-hydroxy-3-naphthoic acid, sulfonation also took place, and with an

equimolecular ratio of hydroxy compound and oxidizing agent, the yield of sulfonic acid was 15% of the amount of hydroxy compound used.

Silver nitrate was also used as oxidizing agent, as well as silver oxide, ferric chloride, and copper sulfate; the experiments were performed with 2-hydroxy 3-naphthoic acid. With silver nitrate, the ratio of $Ag^{\cdot}$:SO_3'':hydroxy compound was 2:3:1. In one experiment, the hydroxy compound was added to a mixture of silver nitrate and sulfite, and the mixture was then boiled; in another, a solution of silver nitrate was added to the boiling solution of sulfite and hydroxy compound. In both cases, practically complete reduction of the silver salt resulted, but sulfonation took place to a negligible degree. Upon substituting silver oxide for the silver nitrate, 19% of the hydroxy compound formed sulfonic acid.

With ferric chloride, using a ratio of $Fe^{\cdots}$:SO_3'':hydroxy compound equal to 2:3:1, and the same experimental conditions as for silver nitrate, 39 and 23% respectively of the hydroxy compound was sulfonated.

With copper sulfate and a ratio of $Cu^{\cdot\cdot}$:SO_3'':hydroxy compound of 2:6:1, with the same conditions as before, the yield of sulfonic acid reached 24 and 50%; in contradistinction to what was found with ferric chloride, better results were obtained with gradual addition of the oxidizing agent.

The experiments showed that not all the oxidizing agents which change sulfite into sulfate are capable of transforming the hydroxy compounds into sulfonic acid, and that oxidizing agents which give a great deal of dithionate may also lead to the formation of sulfonic acids. This is in accord with the suggestion, which we give below, about the mechanism of "oxidative" sulfonation.

In the opinion of H. Bassett and A.Henry [4], with oxidizing agents containing easily reduced metallic ions, the formation of sulfate and dithionate takes place by way of selfoxidizing-selfreducing complex ions like $[Fe(SO_3)_3]'''$, $[Ag(SO_3)_2]'''$, $[Mn(SO_3)_3]''$. With metals which are capable of accepting only a single electron ($Cu^{\cdot\cdot}$, $Fe^{\cdots}$, $Ag^{\cdot}$) singly-charged SO_3' groups are formed in the complex. When two such altered complexes encounter each other, the dithionate ion is formed, and when the complex encounters the original complex SO_3' ion, the electron is given up to the new metal ion, and neutral SO_3 is formed, giving rise to sulfate. One and the same complex leads to sulfate and to dithionate, their ratio being independent of the concentration and acidity, and being determined only by the nature of the metal. When the metal ion is capable of acquiring two electrons ($Pb^{\cdots\cdot}$, $Hg^{\cdot\cdot}$) only sulfate is formed. Manganese dioxide can give both $Mn^{\cdots}$ and $Mn^{\cdot\cdot}$, and lead to the production of both dithionate and sulfate, depending on the sonditions.

Sulfite-complexes of the composition claimed by these authors for $Ag^{\cdot}$ and $Mn^{\cdots\cdot}$ are unknown; that for $Fe^{\cdots}$ is generally denied [10]. The possibility of forming complex ions saturated with SO_3 residues is improbable, in a reaction of this kind. Frequently, the total number of anions that go to form the complex ion is less not only than the coordination number of the metal, but than its valence. Thus, the complex which is obtained in the reaction of ferric salts with thiosulfate, and leads to the formation of tetrathionate, has the composition $[Fe \cdot S_2O_3]^{\cdot}$ [11]. The composition of the complexes is often determined by the ratio of the components; thus, ferric salts and sodium hypophosphite, depending on the amount of the latter, give:

$$[Fe_3(OH)(H_2PO_2)_6]^{\cdot\cdot} \quad \text{and} \quad [Fe(H_2O)(H_2PO_2)_5]'' \text{ [12].}$$

A.K.Babko [13] has shown that in the reaction of $Fe^{\cdots}$ with CNS', depending on the concentration of CNS', there is formed in solution a series of complexes:

$$[Fe(CNS)_n]^{m(+)} \text{ , where } n = 1, 2, 4, 5, \text{ and } m = 3 - n.$$

while with an excess of Fe··· ions, $[Fe_2(CNS)]^{\cdot\cdot\cdot}$ is formed; neighboring forms of complexes are in equilibrium. When Fe··· and F' form complexes, the first form is $[Fe{\cdot}F]^{\cdot\cdot}$ [14]. E.M.Price [15] and A.L.Zaides [13] have shown that in the reaction of sodium sulfite with chromium sulfate, the stepwise complex formation increases as the value of the ratio $SO_3'' : Cr^{\cdot\cdot}$ is increased, not coming to an end even with a ratio of 50:1. The data given above on the oxidation of sulfite with copper sulfate and ferric chloride are in contradiction to the claim of H. Bassett and A. Henry about the ratio of dithionate and sulfate being independent of the concentration and acidity. The claim of these authors that lead dioxide gives only sulfate is correct only for the oxidation of sulfurous acid; with sulfites, large amounts of dithionates are formed [17].

In our opinion, the transition of SO_3'' ions into sulfate and dithionate takes place according to the scheme:

$$S_2O_8'' \longleftarrow B \longleftarrow SO_3'' \longrightarrow A \longrightarrow SO_4'',$$

where (A) and (B) are different complexes, of which one leads to sulfate and the other to dithionate. The oxidation of SO_3'' to SO_4'' is represented as due to the formation of a molecule of SO_3 inside the complex ion (A), followed by decomposition of the ion. For example:

$$aMe^{n(+)} + bSO_3'' \longrightarrow [Me_a^{n(+)} (SO_3'')_b] \longrightarrow$$

$$\text{(I)}\ [Me_{a-1}^{n(+)} : Me^{(n-2)+} (SO_3'')_{b-1} \cdot SO_3]$$

or

$$\text{(II)}\ [Me_{a-2}^{n(+)} \cdot Me_2^{(n-1)+} \cdot (SO_3'')_{b-1} \cdot SO_3].$$

Here Me is the n-valent complex forming metal ion, and a equals 1, 2, and 3. With a metal ion capable of accepting 2 electrons at once (Mn····, Pb····, Hg··, and perhaps Cu··), the reaction follows course (I); with an ion capable of accepting a single electron (Ag·, Cu··, Fe···, Mn···), the reaction goes according to mechanism (II). The transformation of the complex (B) can be indicated in the following way:

$$[Me_c^{n(+)} \cdot (SO_3'')_d] \longrightarrow [Me_{c-1}^{n(+)} \cdot Me^{(n-1)+} \cdot (SO_3'')_{d-1} \cdot (SO_3')],$$

and the formation of the dithionate results from the dimerisation of SO_3' residues from two complexes. The possibility is not excluded that in some cases the formation of S_2O_8'' may also proceed inside the complex ion. Having learned the stepwise character of complex formation, we must assume that the ratio d:c (in complex B) is greater than the ratio b:a (in complex A).

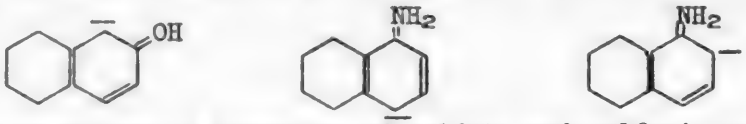
The transformation of SO_3'' ion into neutral sulfur trioxide may be regarded not as an isolated act, but as related to the preliminary hydration of the SO_3'' ion. For the sake of simplicity, it may be indicated by the scheme:

$$[Me^{n(+)} : SO_3''] + H_2O \longrightarrow [Me^{n(+)} \longleftarrow : SO_3''] \longrightarrow$$

$$\longrightarrow Me^{(n-2)+} + H : \underset{\cdot\cdot}{\overset{SO_3}{O}} : H (\longrightarrow H_2SO_4) \qquad H : \underset{\cdot\cdot}{\overset{\uparrow}{O}} : H$$

The donation of electrons by the SO_3'' ion to the metal ion is made easier by the attraction of the sulfur trioxide formed for the electrons of the oxygen in the water molecule. As electron donors for the discharged SO_3'' ions, aquo and hydroxy groups already present in the complex ion may also serve. The same complex acts as a sulfonating agent. The mechanism of the sulfonation reaction does not differ

from the mechanism of sulfate formation, the electron donors here being either the amino groups in amino compounds or the negative carbon atoms in phenols or amines:



This sort of mechanism of formation of sulfate and sulfonic acids is applicable also to mercury sodium sulfite $[Hg(SO_3)_2]Na_2$, as well as to hydroxylamine disulfonate $[HON(SO_3)_2]K_2$ and nitrosulfate $[(NO)_2SO_3]K_2$. The selective sulfonating abilities of these three compounds with regard to hydroxy amino compounds depends on the possibility of the nuclei of the latter entering into a complex, on the tendency of a neutral atom of the complex to acquire electrons, and on the activity of the electrons in one or another part of the molecule of the new component in the complex.

"Oxidative" sulfonation, at least with regard to metal compounds, nitrite, and nitric oxide, is no different in principle from the formation of sulfuric acid derivatives by means of compounds containing bound sulfur trioxide, such as, for example, potassium pyrosulfate, salts of chloropyrosulfuric acid (NaS_2O_6Cl), fluorosulfonates, the esters of chlorosulfonic acid, tri-substituted sulfamido acids ($R_3\overset{+}{N}-\overset{-}{SO_3}$), aminosulfonic acid and its derivatives $[NH(SO_3NH_4)_2$, $N(SO_3K)_3$, $ArNH-SO_3NH_4$, $NH_2-CO-NH-SO_3H]$, hydroxylamine-O-sulfonic acid, products of the addition of SO_3 to dioxane, acylsulfuric acids, dialkyl sulfates, etc. These compounds are unstable to water, and have a tendency to give up SO_3 to other organic and inorganic compounds which contain free pairs of electrons. The reaction usually takes place in the absence of water, but it is sometimes possible also in aqueous medium. Thus, in a series of experiments with potassium pyrosulfate, potassium and ammonium fluorosulfonates, the methyl and ethyl esters of chlorosulfonic acid, and trisubstituted sulfamido acids (for example, $C_5H_5\overset{+}{N}-\overset{-}{SO_3}$) [18] the reaction with phenols in aqueous solution gave their sulfuric acid esters; the reaction with ammonia and with primary and secondary amines gave N-sulfonic acids; the reaction with tertiary amines gave trisubstituted sulfamido acids; with sulfite, dithionate; with ammonium fluoride, fluorosulfonate; with sulfohydrate, thiosulfate. According to P. Baumgarten, pyrosulfate has the structure $[SO_4(SO_3)]K_2$, and he explains the reactions just citedas due tothe removal of sulfur trioxide by substances more capable of holding it than is K_2SO_4. A similar explanation may be given in other cases as well. The sulfonating action of aminosulfonic acids, observed only in the absence of water, is pictured as the transfer of sulfur trioxide from its anhydrous form $H_3\overset{+}{N}-\overset{-}{SO_3}$ [19], and the sulfonating action of dimethylsulfate, according to V.N. Belov and I.V.Machinsky [20] is explained by its decomposition into $(CH_3)_2O$ and SO_3. Because of the tendency of concentrated sulfuric acid to transfer sulfur trioxide to HF, NH_4F, pyridine, and, as A.M.Lukin and G.B.Zavarikhina have found [21], to polycycloketones, we may represent even the usual process of sulfonation with sulfuric acid as a transfer of sulfur trioxide to the electron doublet of the polarized double bond of the carbons of the aromatic nucleus. This viewpoint is very close to what V.A.Izmailsky [3] has suggested.

In consideration of everything that has been said above, we see no great difference between the mechanisms of "oxidative" sulfonation and the usual kind.

EXPERIMENTAL

The experiments were carried out in a three-necked flask with stirrer, reflux condenser, and thermometer, and where it was necessary, with a dropping funnel as well. The 2-naphthol-4-sulfonic acid, 2-naphthol-6-sulfonic acid, 2-naphthol-7-sulfonic acid, and 2-naphthol-3,6-disulfonic acid were used in the form of their sodium

salts, which according to analysis by conjugation with p-diazotcluene were 93.2, 87.2, 93.9, and 86.1%; all these were free of isomers and mineral salts.

The action of permanganate on sulfite and derivatives of 2-naphthol. In these experiments, the sodium sulfite used contained 43.02% Na_2SO_3 and 6.19% Na_2SO_4. The potassium permanganate solution had 1 mole of $KMnO_4$ in 3812 ml.

The solution of 0.04 mole of sodium salt of naphtholsulfonic acid and 0.1 mole of sulfite in 200 ml of water was heated to 70°, and 75 ml of permanganate solution (0.01968 mole) was added, with stirring, in a 30 minute period. Upon reduction to manganese dioxide, this amount of permanganate was capable of changing 0.02592 mole of sulfite into sulfate. After 10 minutes of stirring at 70°, the precipitate of manganese dioxide was filtered off and washed with water, and the filtrate was analyzed by the method described earlier; the remaining sulfite was determined, as well as the amount of sulfate formed, and the amount of unchanged sulfonic acid and the product of its sulfonation. It was shown in preliminary experiments that the products of the oxidation of naphtholsulfonic acid by permanganate, obtained under similar conditions, but in the absence of sulfite, did not absorb iodine in acid medium and did not interfere with the determination of sulfite. The experimental data are given in a table below. In experiment 1, a solution of sulfite alone was oxidized.

No. of expt.	2-Naphthol sulfonic acid	sulfite oxidized in %	Distribution of oxidized sulfite (in % of part oxidized)			Yield of sulfonic acid based on amount of substance at start (in %)	
			Sulfate	Sulfonic acid	Sulfate + sulfonic acid	of total quantity	of amount that reacted
1	–	39.25	94.26	–	94.26	–	–
2	2-Naphthol-6-sulfonic acid	30.31	78.32	14.46	92.78	10.96	46.01
3	2-Naphthol-7-sulfonic acid	29.56	69.45	23.05	92.50	17.03	63.13
4	2-Naphthol-3,6 disulfonic acid	31.90	69.05	26.56	95.61	21.17	55.13
5	2-Naphthol-4-sulfonic acid	31.11	65.82	28.15	93.97	21.89	58.08

Similar experiments were carried out with the sodium salt of 2-hydroxy-3-naphthoic acid. After removal of the manganese oxides, the solution was acidified and 0.03062 mole of unchanged hydroxynaphthoic acid was removed from the filtrate; the filtrate was then concentrated and potassium chloride added. Needles of the potassium salt of 1-sulfo-2-hydroxy-3-naphthoic acid precipitated. The yield of sulfonic acid, determined by the amount of hydroxynaphthoic acid formed after hydrolysis, was 0.0047 mole.

The action of hydrogen peroxide and iodine on sulfite and 2-naphthol-7-sulfonic acid. In these experiments, the sodium sulfite used contained 43.02% Na_2O_3 and 6.19% Na_2SO_4; the hydrogen peroxide contained 2.762 g H_2O_2 and 0.0063 g H_2SO_4 in 10 ml; the iodine solution was 1 N (K = 0.9826).

A solution of 0.04 mole of naphtholsulfonic acid and 0.1 mole of sulfite in 200 ml of water was heated to 50°, and a solution of 5 ml of hydrogen peroxide in

45 ml of water was added in a 35 minute period. The amount of sulfite that was oxidized and completely changed to sulfate was 40.53%; the naphtholsulfonic acid was completely unchanged.

The experiments with iodine were carried out similarly. In the first experiment, the amount of iodine taken was that necessary to oxidize 24.56% of the sulfite, i.e., 50 ml. While the iodine was being added, the solution became cloudy. The sulfite that reacted amounted to 31.42%, the sulfite transformed into sulfate, 30.73%. No formation of disulfonic acid was found. The increased consumption of the sulfite could be explained, on the one hand, by the autoxidation of the sulfite, which was catalyzed by I' ions, and on the other, by the formation of sulfur according to the equation: $3H_2SO_3 = 2H_2SO_4 + S + H_2O$.

In the experiment in alkaline medium, 0.06 g-atom of iodine (61.1 ml) was used, and 0.06 mole of caustic soda was added to the solution of naphtholsulfonic acid and sulfite. The amount of sulfite that reacted was 0.03186 mole, but during the precipitation of $BaSO_4$, further oxidation of the sulfurous acid took place, and the amount of sulfate was 0.035 mole. No naphtholdisulfonic acid was found.

The action of persulfate on sulfite and 2,7- and 2,4-naphtholsulfonic acids. In these experiments, potassium persulfate (purified for analysis) was used, with a preliminary determination of the amount of active oxygen and the amount of sulfate formed during reduction; the sodium sulfite had 42.71% Na_2SO_3 and 6.50% Na_2SO_4.

In the solution, 0.02 mole of 2-naphthol-7-sulfonic acid and 0.1 mole of sulfite in 200 ml of water were heated to 30°; 5.41 g (0.02 mole) of persulfate was added all at once (the temperature of the liquid immediately rose by 10°). The solution was heated to 50°, and agitated at this temperature for 2 hours. The amount of sulfite oxidized was 22.80%, and of this 95.26% formed sulfate. In a similar experiment, the persulfate was added at 50°, and the solution maintained at 85° for 2 hours. In this case, 23.40% of the sulfite was oxidized, and 95.23% of it formed sulfate.

An experiment with 2-naphthol-4-sulfonic acid was carried out similarly at 85°. The sulfite oxidized was 22.66%, and of this 94.70% went to form sulfate. In all these experiments, the monosulfonic acids remained unchanged.

The action of silver nitrate, silver oxide, ferric chloride, and copper sulfate on sulfite and 2-hydroxy-3-naphthoic acid. The sodium salt of 2-hydroxy-3-naphthoic acid used was 98.88% (by iodometric analysis); the solution of sodium bisulfite contained 1 mole of $NaHSO_3$ in 532.8 ml., and the solution of caustic soda 1 mole in 114.7 ml.

At the end of the experiments, the reaction mixture was filtered, the precipitate washed with water, and the filtrate analyzed as previously described. The amounts of unsulfonated hydroxy compounds and of sulfonic acids formed were determined.

Below are given the data on the amounts of 2-naphthol, 1-sulfo-2-hydroxy-3-naphthoic acid, and 2-hydroxy-1-sulfonic acid formed, calculated on the basis of the 2-hydroxy-3-naphthoic acid.

Silver Nitrate. 1. To a mixture of 39.95 ml (0.075 mole) of bisulfite and 8.6 ml (0.075 mole) of caustic soda at room temperature, a solution of 8.54 g (0.05 mole) of 99.47% silver nitrate in 45 ml of water was added over a 30 minute period; then a solution of 5.3105 g (0.025 mole) of the sodium salt of hydroxynaphthoic acid in 85 ml of water was heated to 68°, and added. The mixture was boiled for 2 hours. The white precipitate which had been formed upon mixing the silver nitrate with sulfite acquired a grayish color even at 80°. The precipitate was filtered off at the end of the experiment, and dried in air; it weighed 5.31 g, and contained 98.1% silver. This was 96.47% of the calculated amount. Upon treatment

of the filtrate, there was obtained 4.3472 g of 99.1% 2-hydroxy-3-naphthoic acid (m.p. 218.5°); from this filtrate, 0.1034 g of additional unsulfonated hydroxy compound was obtained. Of the amount of hydroxy compound used, 93.85% was recovered unsulfonated.

2. A solution of 5.3105 g of the sodium salt of 2-hydroxy-3-naphthoic acid, 39.95 ml of bisulfite, and 8.6 ml of caustic soda in 85 ml of water was heated to the boiling point, and a solution of 8.54 g of silver nitrate in 45 ml of water added during a period of 1 hour. The mixture was boiled for an additional hour. Upon treatment of the reaction mixture, 5.2965 g of 98.6% silver was obtained, i.e, 96.83% of the calculated amount, and 4.467 g of hydroxy compound, i.e., 95.04% of the amount taken. In both cases, after removal of the unsulfonated hydroxy compounds, concentration, and addition of potassium chloride, there precipitated from the aqueous solutions a small quantity of a crystalline material, with the properties of 1-sulfo-2-hydroxy-3-naphthoic acid.

Silver Oxide. A solution of 5.3105 g of the sodium salt of hydroxynaphthoic acid, 39.95 ml of bisulfite, and 8.6 ml of caustic soda in 85 ml of water was heated to 90-94°, and a paste of freshly precipitated silver oxide, obtained from 8.9672 g (0.0525 mole) of silver nitrate and 45 ml of water, was added over a 5 minute period. The mixture was then boiled 1½ hours. The liquid, dark brown in color, gradually became light yellow, and silver powder settled on the bottom of the flask. Upon treatment of the reaction mixture, 5.5502 g of 98.63% silver was obtained, i.e., 96.65% of the calculated amount; analysis of the filtrate gave 3.334 g of unsulfonated hydroxy compounds and 0.8948 g of sulfonic acid. The yield of sulfonic acid amounted to 19.04% of the amount of hydroxy compound used, and 65.51% of the amount that had reacted. The separation of the potassium salt of 1-sulfo-2--hydroxy-3-naphthoic acid was carried out in the manner indicated above.

Ferric Chloride. 1. To 39.95 ml of bisulfite neutralized with 8.6 ml of caustic soda at room temperature, 14.0 ml of a ferric chloride solution (0.05 mole; 1 mole equals 280 ml) was added in a period of 8 minutes. This was diluted with 25 ml of water, and a solution of 5.3105 g of the sodium salt of hydroxynaphthoic acid in 85 ml of water was then added. The mixture was boiled for 1 hour. Upon the addition of ferric chloride to the sulfite, an orange precipitate first separated out; this quickly dissolved to give a dark red color. After the addition of ¾ of the solution, a voluminous orange-red precipitate again formed. This turned black upon the addition of the hydroxynaphthoic acid solution. At the end of the reaction, the mass had a brown color, and the odor of sulfur dioxide. The precipitate was filtered off and washed with weak alkali; the filtrate contained 1.5493 g of unsulfonated hydroxy compounds; 1.02 g of the hydroxynaphthoic acid had formed 1-sulfo-2-hydroxy--3-naphthoic acid, and 0.80 g had formed 2-naphthol-1-sulfonic acid. The yield of sulfonic acid was 38.7% based on the amount of hydroxynaphthoic acid used, and 57.8% based on the amount which had reacted.

2. To a solution containing 5.3105 g of the sodium salt of hydroxynaphthoic acid, 39.95 ml of bisulfite, and 8.6 ml of caustic soda in 85 ml of water at 90-95°, there was added 14 ml of ferric chloride, diluted with 30 ml of water. At the end of the experiment, a strong odor of sulfur dioxide was noted. Of the hydroxy-naphthoic acid, 2.425 g remained unchanged, 0.759 g formed 2-naphthol, 0.563 g gave 1-sulfo-2-hydroxy-3-naphthoic acid, and 0.52 g gave 2-naphthol-1-sulfonic acid. The yield of sulfonic acid was 23.0%, based on the amount of hydroxynaphthoic acid used, and 71.4% based on the amount that had reacted.

Copper Sulfate. 1. To a mixture of 79.9 ml (0.15 mole) of bisulfite and 17.2 ml (0.15 mole) of caustic soda at room temperature, a solution of 12.6 g (0.05 mole) of 99.07% copper sulfate in 40 ml of water was quickly added. This was followed by a solution of 5.3105 g (0.025 mole) of the sodium salt of hydroxynaphthoic acid in 65 ml of water. The mixture was heated for 1 hour. Upon mixing the copper sulfate

with the sulfite, a greenish-yellow flocculent precipitate was formed; after the addition of the hydroxynaphthoic acid, this became dark brown, and upon heating it turned light brown and crystalline. At the end of the experiment, a faint odor of sulfur dioxide was noted. It was found by analysis that 3.413 g of the hydroxynaphthoic acid remained unchanged, 0.0424 g had gone to form 2-naphthol, 0.9523 g had formed 1-sulfo-hydroxy-3-naphthoic acid, and 0.1758 g had formed 2-naphthol-1-sulfonic acid. The yield of sulfonic acid was 24% based on the amount of hydroxynaphthoic acid taken, and 90.6% based on the amount reacted.

2. To a boiling solution of 5.3105 g of the sodium salt of hydroxynaphthoic acid, 79.9 ml of bisulfite, and 17.2 ml of caustic soda in 80 ml of water, a solution of 12.6 g of copper sulfate in 45 ml of water was added over a 45 minute period. The mixture was boiled an additional hour. At the beginning of the addition of the copper sulfate, a brown precipitate formed, and then went into solution again. Later, an insoluble crystalline precipitate of a weak brownish color was formed. Of the hydroxynaphthoic acid, 2.2311 g remained unchanged, 0.0195 g formed 2-naphthol, 2.192 g gave 1-sulfo-2-hydroxy-3-naphthoic acid, and 0.1754 g gave 2-naphthol-1-sulfonic acid; the yield of sulfonic acid was 50.4% based on the amount of hydroxynaphthoic acid taken, and 96.7% based on the amount which had reacted.

The crystalline precipitate which had been formed in both experiments quickly took on a green color. Under the action of sulfuric acid, it evolved sulfur dioxide, and gave copper sulfate and metallic copper. Under the action of alkali, it gave a yellowish precipitate which was soluble in ammonia; it was probably the double sulfite of sodium and cuprous copper.

The action of 1,2-naphthoquinone-4-sulfonic acid on sulfite and on 2-hydroxy-3-naphthoic acid. A solution of 0.05 mole of the sodium salt of 2-hydroxy-3-naphthoic acid, 107 ml (0.2 mole) of bisulfite, and 5.7 ml (0.05 mole) of caustic soda in 65 ml of water was heated to 95°; over a 30 minute period, 13.0 g (0.05 mole) of the dry sodium salt of 1,2-naphthoquinone-4-sulfonic acid was added in small portions. The yellow-brown solution formed was boiled for 1½ hours. After the usual treatment, 7.31 g of hydroxynaphthoic acid (m.p. 218.5°) was obtained; in the filtrate from this, there were found 0.11 g of unchanged hydroxynaphthoic acid, as well as 0.2 g which had been converted into 2-naphthol, 0.92 g into 1-sulfo-2-hydroxy-3-naphthoic acid, and 0.51 g into 2-naphthol-1-sulfonic acid. (It was determined in advance that the presence of 1,2-naphthohydroquinone-4-sulfonic acid, formed from the quinonesulfonic acid, did not affect the accuracy of the determination of sulfonic acid obtained from hydroxynaphthoic acid by the method of analysis used.) The yield of sulfonic acid amounted to 15.2% based on the amount of hydroxynaphthoic acid used, and 80.3% based on the amount which had reacted.

Qualitative experiments showed that mixtures of bisulfite with 1-nitroso-2-naphthol or 2-nitroso-1-naphthol-4-sulfonic acid had a weak sulfonating tendency.

SUMMARY

1. A study has been made of the relation of several derivatives of 2-naphthol to sulfite which is undergoing oxidation by iodine, hydrogen peroxide, potassium persulfate, permanganate, 1,2-naphthoquinone-4-sulfonic acid (oxidizing agents which form sulfate), silver nitrate, ferric chloride, and copper sulfate (oxidizing agents which give a large quantity of dithionate).

2. Of the oxidizing agents which give sulfate, only permanganate and the quinonesulfonic acid gave sulfonic acids. The other oxidizing agents gave sulfonic acids in quantities which depended on the nature of the oxidizing agent, the structure of the sulfonated substance, and the conditions of the reaction; silver oxide gave better results than did silver nitrate.

3. A mechanism has been given for the oxidation of sulfite by metallic compounds to give sulfate and dithionate, and a mechanism for the formation of sulfonic acid during oxidative sulfonation.

4. It has been shown that there is no difference in prinicple between the mechanisms of oxidative sulfonation and sulfonation by compounds containing bound sulfur trioxide.

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THE COLOR OF ORGANIC DYES AND THE PLANAR NATURE OF THEIR MOLECULES I.

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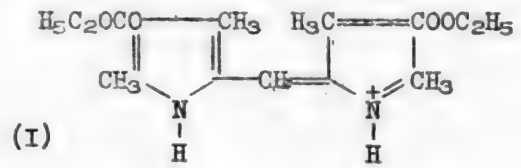
At present it may be considered beyond doubt that the color of every organic dye is related to the resonance between the various possible structures it may have. But resonance makes its appearance only in plane or almost plane systems of atoms. Consequently, we must picture the molecules of dyes, or at least the conjugated chains in the dye molecules, as lying in a single, or almost a single, plane.

The question then arises: what will happen to the color of a dye if we, by one means or another, destroy the planar nature of its molecules, and put difficulties in the way of their resonance structures?

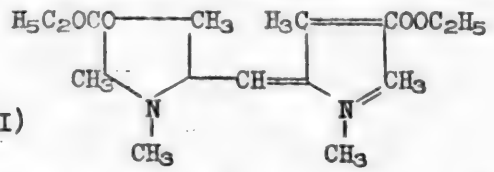
The data which exist in the chemical literature do not give a clear answer to this question. It is known that in the case of trans-α-methylstilbene, in whose molecule the methyl is an obstacle to the existence of the two benzene nuclei in a single plane [1], the region of absorption is displaced, in comparison with trans-stilbene, toward the short-wave direction [2]. There is an even greater displacement in the same direction with trans-α,α'-dimethylstilbene. In the case of cis-azobenzene, the benzene nuclei are turned at an angle of 50° with regard to each other, while trans-azobenzene is almost plane [3]. Corresponding to this difference, cis-azobenzene absorbs in a region of shorter waves than does trans-azobenzene.

However, from the other side, Scheibe showed in 1941 [4] that in the case of several monomethinecyanines of the quinoline series, the substitution of methyl by ethyl is related to steric hindrance, and apparently to some extent deprives the molecule of its planar structure, resulting in a displacement of the absorption band in the long-wave direction. Especially interesting data were obtained by Brunnings and Corwin [5], who synthesized several dipyrrylmethenes and showed that the substitution in compound (I):



(I)

of the two hydrogen atoms by methyl groups, giving compound (II):



(II)

results in a displacement of the absorption band toward the red by 40 mμ, while simultaneously, the intensity of absorption decreases. There is no difficulty

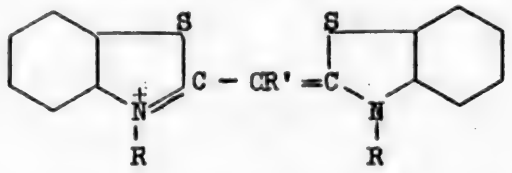
in confirming, by means of models, the fact that the methyl groups on the hetero atoms of nitrogen in compound (II) are at a shorter distance from each other than they can be in a single plane. The destruction of the coplanar relation of the pyrrol nuclei is apparently, in the opinion of the authors, due to the deformation of the valence angles, and is the cause of the displacement of the absorption band in the long-wave direction.

A similar phenomenon was observed by Ellingson and Corwin [6] for N-methyl-etioporphyrin [8], and by Vittum and Brown for methylated indoaniline dyes [7].

In 1946 we synthesized a series of thiocarbocyanine dyes containing phenyl groups upon the hetero atom of nitrogen. In these syntheses, we observed a remarkable displacement of the absorption band toward the red end of the spectrum in those compounds which had alkyl or aryl [8] groups in the neighborhood of the phenyl groups. At first we could find no explanation for this phenomenon, and were even ready to consider that these deeply colored compounds actually had a different structure from that which we had ascribed to them on the basis of analysis and method of preparation, all the more so as they were decolorized by alkali [8] with unusual ease.

However, we soon synthesized monomethinecyanines of the same type, and after investigating the absorption spectra of these simpler compounds, we arrived at the conclusion that the cause of the anomalously deep color was the impossibility of these compounds having a plane structure of the molecule.

Let us consider the compounds in whose absorption curves we noted the indicated steric effects. In Table 1 are given the absorption maxima and the molecular extinction of the monomethinethiocyanines we obtained, with the general formula:



On comparing compounds (I) and (II), we see that the substitution of the hydrogen atom in the methine group of the first by methyl very strongly displaces the absorption maximum in the long-wave direction, and decreases the intensity of absorption. The same thing is observed on comparing compounds (III), (IV), and (V). In those monomethinecyanines containing phenyl radicals on the nitrogen hetero atoms, the substitution of the hydrogen atom in the methine group by methyl displaces the absorption maximum by 31 mμ in the long-wave direction. The substitution of the methyl group by ethyl gives an additional displacement of 41 mμ in the same direction. The deepening of the color is accompanied by a sharp decrease in the intensity of absorption, which is typical of steric effects [10].

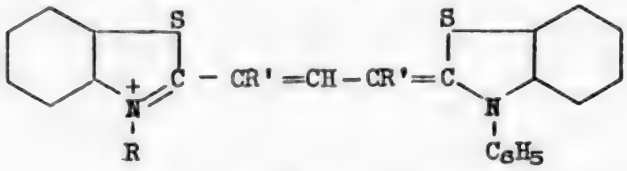
TABLE 1

Compound	R	R'	λ_{max} in mμ	$E_{max} \cdot 10^{-4}$
I....	CH_3	H	422	8.1
II....	CH_3	CH_3	465	6.0
III....	C_6H_5	H	429	7.5
IV....	C_6H_5	CH_3	460	3.5
V....	C_6H_5	C_2H_5	501	2.1

From Fig. 1, in which the structure of the cation of dye (I) is shown with approximately correct valence angles and atomic radii [11], it can be seen that the methyl groups, and to an even greater degree the phenyl, attached to the nitrogen hetero atoms leave little room for a radical which substitutes for the hydrogen of the methine group. Fig. 1 gives the cis-form of thiocyanine. Steric hindrance does

not prevent the transition to the trans-form.

In Table 2 is listed a series of trimethinecyanines we have synthesized. These contain one or two phenyl groups attached to the nitrogen hetero atom, and have the general formula:



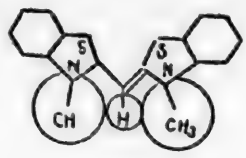


Fig. 1.

It is obvious from Table 2 that in the trimethinecyanines, the methyl radical in the chromophore neighboring the ethyl radical upon the nitrogen hetero atom (VII) has little influence on the absorption. It is clear that the influence of the methyl group is considerably strengthened in the neighborhood of phenyl (VIII and IX), and that when we introduce a second methyl group alongside the second phenyl (X), the absorption maximum undergoes a displacement of 30 mμ toward the red, while the intensity of absorption is cut in half.

TABLE 2

Compound	R	R'	R''	λ_{max} in mμ	$E_{max} \cdot 10^{-4}$
VI....	C_2H_5	H	H	560	14.8
VII....	C_2H_5	CH_3	H	562	11.0
VIII....	C_2H_5	H	CH_3	570	14.8
IX....	C_6H_5	CH_3	H	572	15.0
X....	C_6H_5	CH_3	CH_3	602	8.8

Fig. 2 shows schematically the structure of the simplest thiocarbocyanine. The substitution of the hydrogen atoms in the neighborhood of the methyl radicals by alkyl, apparently already causes a deformation of the valence angles, but is still possible without destruction of the planar nature of the molecule. If, however, it is not methyl radicals, but phenyl which are attached to the nitrogen hetero atoms, the simultaneous substitution of both hydrogen atoms by alkyl makes a plane structure of the molecule of the compound impossible. In the case of substitution of only one hydrogen atom by alkyl (VIII or IX), a coplanar trans-form is possible.

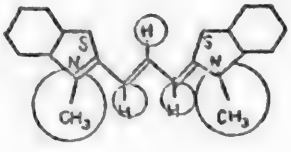
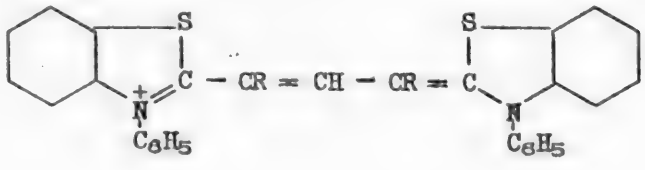


Fig. 2.

TABLE 3

Compound	R	λ_{max} in mμ	$E_{max} \cdot 10^{-4}$
XI...	H	565	15.5
X...	CH_3	602	8.8
XII...	C_2H_5	600	6.6
XIII...	C_6H_5	601	4.0
XIV...	α-$C_{10}H_7$	592	9.5
XV...	β-$C_{10}H_{11}$	590	

In Table 3 are listed the symmetrical trimethinecyanines with two phenyl radicals attached to the nitrogen hetero atoms, and with two substituents near them. The general formulas are:



We see that the methyl groups have already fully resulted in producing steric effects. Their substitution by radicals of greater volume – phenyl, α-naphthyl, or β-tetralyl, does not strengthen the effect.

The phenomenon which characterizes steric hindrance – the displacement of the absorption band toward the red, and the decrease in absorption intensity – may also be observed in the case where methyl radicals are attached to the nitrogen hetero atoms, while two substituents of large volume are in the chromophore in their neighborhood. In Fig. 4 are given examples of such varieties in dyes with the general formula:

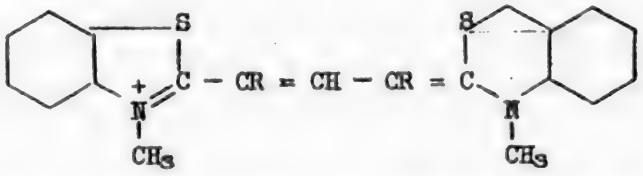


Table 4 makes especially clear the effect of steric hindrance upon the values of the molecular extinction. The larger the volume of the radical introduced into the 8- or 10- position, the less the extinction. The same sort of parallelism between the volume of the radicals and the values of displacement of the absorption

TABLE 4

Compound	R	λ_{max} in mμ	$E_{max} \cdot 10^{-4}$
XVI...	H	558	14.0
XVII...	CH_3	570	7.0
XVIII...	C_6H_5	580	4.1
XIX...	α-$C_{10}H_7$	568	3.7
XX...	β-$C_{10}H_{11}$	578	2.1

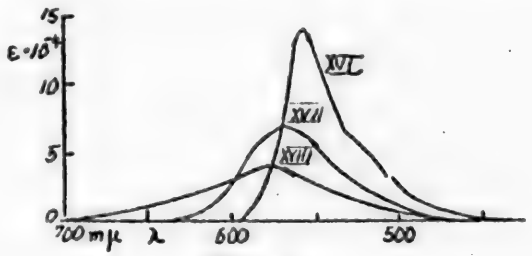


Fig. 3

maximum has not been observed. We must, however, remember that steric hindrance is reflected not only in the position of the maximum, but also in the form of the absorption curve. Starting with a narrow and sharp curve, with a very steep slope on the side of the red portion of the spectrum for preparation (XVI), the absorption curve for its derivatives (XVII) and (XVIII) becomes continually broader and more extended (Fig. 3). It is interesting to note that with compound (XVIII) the displacement of the absorption maximum is less than with its isomer (X) (580 and 602 mμ, respectively). Possibly, the compounds of Table 4 are capable of existing in a trans-trans form (Fig. 4), which is impossible for the compounds of Table 3.

I.K.Ushenko has synthesized two series of peculiar thiocarbocyanine dyes, containing hydrocarbon rings in the chromophore [12]. For each compound with alkyls upon the nitrogen hetero atoms, he obtained an analog with phenyl groups in the same positions. Table 5 lists the absorption maximum and the molecular extinction of these compounds with the general formula :

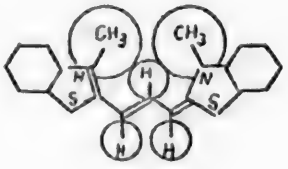


Fig. 4

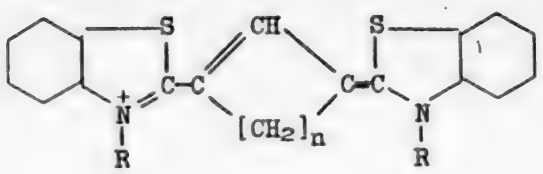
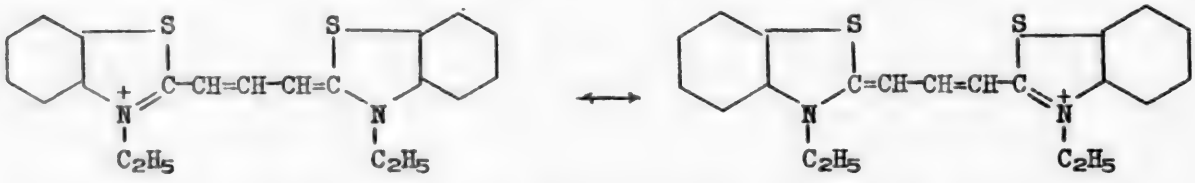


TABLE 5

Compound	n	R	λ_{max} in mμ	$E_{max} \cdot 10^{-4}$
XXI...	1	C_2H_5	558	14.8
XXII...	1	C_6H_5	568	7.4
XXIII...	2	C_2H_5	601	17.4
XXIV...	2	C_6H_5	623	6.5
XXV,..	3	CH_3	565	13.0
XXVI...	3	C_6H_5	598	10.5
XXVII...	4	CH_3	575	6.1
XXVIII...	4	C_6H_5	603	8.1
XXIX...	5	CH_3	563	5.6
XXX....	5	C_6H_5	601	2.5
XXXI...	6	CH_3	558	6.2
XXXII...	6	C_6H_5	600	2.5

In the compounds of Table 5, the same rules hold as have already been noted above. Compounds with phenyl groups upon the nitrogen hetero atoms absorb much farther toward the red end of the spectrum than compounds with methyl or ethyl groups. The molecular extinction of the phenyl derivatives has a much lower value (except for compound XXVIII).

All the cyanine dyes which are considered in this communication are compounds of symmetrical or almost symmetrical structure. Their basic resonance structures, such as:



are of equal energy content. The destruction of the coplanar relation of the heterocyclic nuclei in the dye molecule decreases the resonance of the interaction of the structures (the "conjugation" of the structures, according to Ferster [13]). If these structures are energetically equivalent, the decrease in resonance interaction will lead to a drawing together of the levels of the basic and excited states of the molecule, i.e., to absorption in the longer-wave section of the spectrum. The destruction of the coplanar relation of the heterocycles has the same effect upon the absorption of light by the symmetrical cyanine dyes as a lengthening of the polymethine chain.

The decrease in the resonance interaction of the structures also has another result. Upon destruction of the coplanar relation, just as in the case of lengthening of the polymethine chain, there is a decrease in the resonance energy which stabilizes the molecule of the dye. Therefore the dye, which has a deep color as a result of steric hindrance, is more easily decolorized by alkali and acid than other dyes of the same type. As is well known, [14], the same thing is observed with cyanine dyes which have a long chain.

We must also note that all the cyanine dye compounds described here as having a non-planar structure of the molecule have a very much lower melting point (often half the value) than their plane homologs. The majority of such "non-planar" dyes are by far more soluble in alcohol than the corresponding "planar" compounds. Experiments with trimethine dyes which have large radicals in silver bromide emulsions have shown that they are ineffective photosensitizers. This, obviously, is directly related to the absence of a planar structure.

When the present work was almost completed, and its chief results had been

published [15], an article appeared by Brooker and coworkers which considered the same question [16]. The American authors made absorption curves of cyanine dyes, chiefly of quinoline derivatives, and observed phenomena similar to those that we noted. They also gave explanations similar to ours.

The measurements of absorption curves of the dyes, as carried out in our work, were made with a Bellingham-Stanley spectrophotometer in a solution of ethyl alcohol.

EXPERIMENTAL

Bis-(3-methylbenzothiazole-2)monomethinecyanineiodide (I) was obtained from the methyl iodide of 2-methylbenzothiazole and the methylmethosulfate of 2-methylmercaptobenzothiazole by boiling in absolute alcohol in the presence of anhydrous sodium acetate. After recrystallization from alcohol, there were obtained finely interwoven silky crystals of a lemon yellow color, m.p. 281°, with decomposition (here and later, the temperatures indicated are corrected).

Bis-(3-methylbenzthiazol-2)-8-methylmonomethinecyanine iodide (II) was obtained in the same way from the methyl iodide of 2-ethylbenzothiazole. The yield of unrecrystallized compound was 35% of theory. There were large orange crystals of the monoclinic system, m.p. 237°, with decomposition. Upon heating to 100°, the crystals turned red.

Found %: I 28.30; N 6.15.
$C_{18}H_{17}N_2S_2I$. Calculated %: I 28.10; N 6.20.

Bis-(3-phenylbenzothiazole-2)-monomethinecyanine iodide (III) was obtained by Brooker's method [17], by heating the phenyl-p-toluenesulfonate of 2-methylmercaptobenzothiazole with malonic acid in pyridine. M.p. 315°, with decomposition.

Bis-[3-Phenylbenzothiazole-(2)]-8-methylmonomethinecyanine iodide (IV). 1.2 g of the phenyl-p-toluenesulfonate of 2-methylmercaptobenzothiazole, 1 g of the chlorophenylate of 2-ethylbenzothiazole, and 1 g of anhydrous sodium acetate were heated in 10 ml of absolute alcohol at the boiling point for 1 hour. The dye was precipitated from solution as the potassium iodide. The non-crystalline precipitate was dissolved in acetone and precipitated with ether. After recrystallization from 15 ml of alcohol, the yield was 0.25 g, or 10% of theory. The compound was in the form of small bronze leaves, m.p. 266°, with decomposition.

Found %: I 22.21.
$C_{28}H_{21}N_2S_2I$. Calculated %: I 22.05.

Bis-[3-phenylbenzothiazole-(2)]-8-ethylmonomethinecyanine iodide (V). From 0.86 g of the phenyl-p-toluenesulfonate of 2-methylmercaptobenzthiazole and 1 g of the ethyl iodide of 2-p-propylbenzothiazole, as in the previous case. The heating of the mixture on a boiling water bath was continued for 4 minutes. The compound was precipitated by ether from acetone solution and recrystallized from alcohol. It was obtained in a yield of 0.2 g, or 13% of theory. M.p. 214°.

Found %: I 21.43.
$C_{29}H_{23}N_2S_2I$. Calculated %: I 21.52.

[3-Ethylbenzothiazole-(2)][3-phenylbenzothiazole-(2)]-trimethinecyanine iodide (VI). 0.78 g of the ethyl iodide of 2-methylbenzothiazole, 1 g of the ethyl iodide of 2-(ω-acetanilidovinyl)-benzothiazole, and 3 ml of pyridine were heated to boiling for 15 minutes. The precipitate was washed with ether and recrystallized from alcohol. It consisted of small dark green tablets. Yield. 0.6 g, or 50% of theory, m.p. 243°, with decomposition.

Found %: I 23.65.
$C_{25}H_{21}N_2S_2I$. Calculated %: I 23.51.

[3-Ethylbenzothiazole-(2)][3-phenylbenzothiazole-(2)]-8-methyltrimethinecyanine iodide (VII). 0.32 g of the ethyl iodide of 2-ethylbenzothiazole, 0.5 g of the phenyl iodide of 2-(ω-acetanilidovinyl)-benzothiazole, and 3 ml of pyridine were boiled for 1 hour. After two recrystallizations from alcohol, large crystals with a bronze luster were obtained. Yield 0.35 g, or 60% of theory. M.p. 158°.

Found %: I 22.85.
$C_{26}H_{23}N_2S_2I$. Calculated %: I 22.92.

[3-Ethylbenzothiazole-(2)][3-phenylbenzothiazole-(2)]-10-methyltrimethinecyanine iodide (VIII). From the phenyl chloride of 2-ethylbenzothiazole and the ethyl iodide of 2-(ω-acetanilidovinyl)-benzothiazole in pyridine. The boiling was continued for 50 minutes. After recrystallization from alcohol, large blue-green crystals with a metallic luster were obtained. M.p. 252°.

Found %: I 22.79 22.83.
$C_{26}H_{23}N_2S_2I$. Calculated %: I 22.92.

Bis-[Phenylbenzothiazole-(2)]-8-methyltrimethinecyanine iodide (IX). 0.5 g of the phenyl iodide of 2-ethylbenzothiazole and 0.67 g of the phenyl iodide of 2-(ω-acetanilidovinyl)-benzothiazole were heated in boiling pyridine for 1 hour. After recrystallization from alcohol, large crystals were obtained; yield 0.25 g, m.p. 275°, with decomposition.

Found %: I 21.20.
$C_{30}H_{23}N_2S_2I$. Calculated %: I 21.09.

From the pyridine mother liquid, there was extracted with ether a symmetrical dye without methyl groups in the trimethine chain. The quantity was 0.3 g, m.p. was 277°, and maximum absorption 565 mμ.

Found %: I 21.46.
$C_{28}H_{21}N_2S_2I$. Calculated %: I 21.59.

The synthesis of thiocarbocyanines (X, XI, XII, XIII) has been described in the work of Kiprianov and Ushenko [18].

Bis-[3-phenylbenzothiazole-(2)]-8,10-di-α-naphthyltrimethinecyanine perchlorate (XIV). 1 g of the ethyl iodide of 2-α-naphthylmethylbenzothiazole (obtained by the condensation of the acid chloride of α-naphthylacetic acid with N-phenyl-o-aminothiophenol), 1 g of orthoformic ester, and 4 ml of acetic anhydride were heated at the boiling point for 40 minutes. To the dark blue solution were added 3 ml of alcohol, and then a hot aqueous solution of sodium perchlorate. The precipitate was recrystallized twice from alcohol. Yield 0.27 g (32% of theory). Bronze crystals; m.p. 196-197°.

Found %: N 3.33.
$C_{49}H_{33}O_4N_2S_2Cl$. Calculated %: N 3.43.

Bis-[3-phenylbenzothiazole-(2)]-8,10-di-β-tetralyltrimethinecyanine perchlorate (XV). The dye was obtained by the action of the phenyl iodide of 2-β-tetralyl methylbenzothiazole on orthoformic ester in acetic anhydride. Maximum absorption, 590 mμ. The compound was not separated in pure form. For the preparation of the quaternary salts of 2-β-tetralylmethylbenzothiazole, see below.

Bis-[3-methylbenzothiazole-(2)]-8,10-dimethyltrimethinecyanine iodide (XVII). 1 g of the methyl iodide of 2-ethylbenzothiazole, 1.5 g of orthoformic ester, and 5 ml of pyridine were heated at the boiling point for 45 minutes. Then 15 ml of water was added, and the pyridine neutralized with hydrochloric acid. A bronze-colored precipitate formed. It was filtered off, washed with water, and dried. The unpurified compound weighed 0.18 g. After recrystallization from 80 ml of alcohol, bronze needles were obtained, m.p. 223°, with decomposition.

Bis-[3-methylbenzothiazole-(2)]-8,10-diphenyltrimethinecyanine perchlorate (XVIII). 1 g of the methyl iodide of 2-benzylbenzothiazole (obtained by the condensation of the acid chloride of phenylacetic acid with N-methyl-o-aminothiophenol, followed by treatment with potassium iodide; m.p. 200°, with decomposition), 1 g of orthoformic ester, and 3 ml of acetic anhydride were heated at the boiling point for 1 hour. To the blue solution were added 3 ml of alcohol and a hot solution of sodium perchlorate. The dye which precipitated out was recrystallized twice from alcohol. Yield 0.18 g, or 22% of theory. Fine violet crystals, m.p. 152°, with decomposition.

Found %: N 4.74.
$C_{31}H_{25}O_4N_2S_2Cl$. Calculated %: N 4.76.

Bis-[3-methylbenzothiazole-(2)]-8,10-α-dinaphthyltrimethinecyanine perchlorate (XIX). From the methyl iodide of 2-α-naphthylmethylbenzothiazole (obtained by the condensation of the acid chloride of α-naphthylacetic acid with N-methyl-o-aminothiophenol, followed by treatment with potassium iodide; m.p. 212°, with decomposition), orthoformic ester, and acetic anhydride, as in the previous case. After recrystallization from alcohol, the yield was 29% of theory. Fine violet crystals, m.p. 176°, with decomposition.

Found %: N 4.05.
$C_{39}H_{29}O_4N_2S_2Cl$. Calculated %: N 4.07.

Bis-[3-methylbenzothiazole-(2)]-8,10-di-β-tetralyltrimethinecyanine perchlorate (XX). 1 g of the methyl iodide of 2-β-tetralylmethylbenzothiazole, 0.4 g of orthoformic ester, and 5 ml of acetic anhydride were heated at the boiling point for 1 hour. Then the acetic anhydride was decomposed by boiling with water, and the precipitate of dye was dissolved in alcohol and treated with a solution of sodium perchlorate. The blue crystalline precipitate was recrystallized from aqueous alcohol. Yield 0.18 g, or 25% of theory. M.p. 152°, with decomposition.

Found %: N 3.96.
$C_{39}H_{37}O_4N_2S_2Cl$. Calculated %: N 4.02.

The synthesis of thiocarbocyanines (XXI to XXXII) is described in the work of Ushenko [12]. β-Tetralylacetic acid (1,2,3,4-tetrahydro-6-naphthylacetic acid). β-Chloromethyltetraline was obtained by the chloromethylation of tetraline [19], with a yield 52% of theory; b.p. 139-142° at 11 mm.

The nitrile of β-tetralylacetic acid was obtained by 3 hours boiling of 71 g of β-chloromethyltetraline with 29 g of sodium cyanide in 400 ml of alcohol, diluted with 70 ml of water. The precipitate of sodium chloride was filtered off, the alcohol driven off by heat, and the remaining yellow-brown oil purified by distillation in vacuum. At 178-182° and 15 mm pressure, the nitrile distilled. It was a colorless liquid, quickly turning yellow upon standing. Yield 48.5 g, or 72% of theory.

β-Tetralylacetic acid was obtained by the saponification of 22 g of the nitrile by boiling with a 20% solution of caustic soda for 10 hours in a flask with a stirrer and a reflux condenser. Upon saponification, a layer of oil formed on the surface of the liquid; this consisted of a concentrated solution of the sodium salt of β-tetralylacetic acid, containing unsaponified nitrile, and a small quanity of the amide of β-tetralylacetic acid. When this oil was separated and treated with water, the greater part dissolved, and upon acidification with hydrochloric acid, there precipitated from the solution β-tetralylacetic acid, which had a cream color. Yield of unpurified acid 16.1 g, or 70% of theory. For purposes of purification, the acid was once more dissolved in dilute aqueous alkali, filtered from the admixture of amide, and strongly acidified with hydrochloric acid. Upon rubbing with a glass rod, there precipitated from the transparent solution colorless needle-like

crystals of tetralylacetic acid, m.p. 78°. After several recrystallizations from water, the melting point rose to 85°. An analysis of the acid was made by determining its equivalent upon titration with 0.1 N alkali. The calculated equivalent was 190, that found 198.

From the residues left during the purification of the acid, the amide of β-tetralylacetic acid was obtained. After recrystallization from water, this was in the form of white plates with mother-of-pearl luster, m.p. 142°.

The acid chloride of β-tetralylacetic acid was obtained by the action on the acid of thionyl chloride. The reaction took place with the evolution of heat. The mixture was heated on the water bath until the evolution of gas ceased. The acid chloride was redistilled in vacuum at 5 mm pressure. It had b.p. 143-144°. Yield 78% of theory.

The methyl iodide of 2-β-tetralylmethylbenzothiazole. 2.8 g of β-tetralylacetyl chloride was dissolved in 5 ml of benzene, and to the solution was added 2 g of N-methyl-o-aminothiophenol. The reaction took place with the evolution of heat, and at the bottom of the test tube a viscous yellow mass settled out. After 10 minutes of heating, the benzene solution was poured off, and the precipitate dissolved in water; the part that was insoluble in water was extracted with benzene. To the transparent aqueous solution was added a hot solution of potassium iodide. The crystalline methyl iodide precipitated. After two recrystallizations from water, it was in the form of crystals with a light cream color. M.p. 220°. Yield 72% of theory.

Found %: I 29.95.

$C_{19}H_{18}NSI$. Calculated %: I 30.14.

The syntheses of β-tetralylacetic acid, the quaternary salt of 2-β-tetralylmethylbenzothiazole, and dye (XX) were carried out by student I.A.Sorochan.

SUMMARY

A number of cyanine dyes have been synthesized which contain radicals of large volume in the molecule close together. It has been shown that in these compounds a displacement of the absorption band toward the red part of the spectrum occurs, along with a decrease in the intensity of absorption in comparison with similar dyes not containing substituents. The authors believe that as a result of the accumulation of radicals, the coplanar relation of the heterocyclic nuclei in the molecule of cyanine dyes is destroyed. This results in a decrease in the resonance interaction of the structures (a decrease in the conjugation of the structures) and a drawing together of the basic and excited levels of the molecules.

The destruction of the coplanar relation between the heterocyclic nuclei influences the properties of the cyanine dye in the same manner as the lengthening of the polymethine chain. Along with the displacement of the absorption band to the long-wave region, much easier decolorization is observed of the corresponding dyes by both alkali and acid. The melting point of the 'nonplanar' dye is lower, and the solubility in alcohol greater, than for the corresponding "planar" dyes.

In the experimental section, the synthesis of 15 new thiocyanine dyes has been described.

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THE REACTIONS OF METHYLENE BASES OF THE THIAZOLE SERIES WITH ALKYL HALIDES

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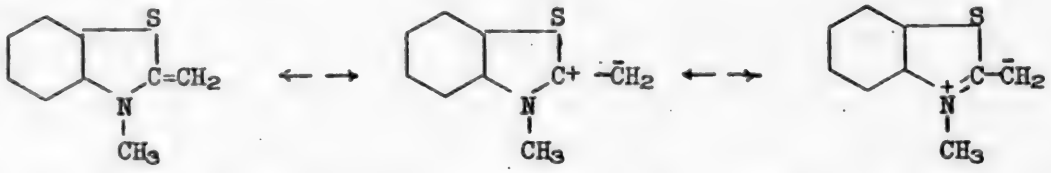
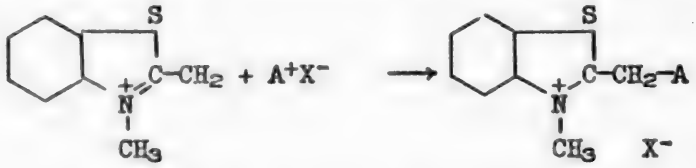
The methylene bases with nitrogen-containing heterocycles are extremely reactive compounds. They react very easily with different kinds of electrophilic reagents – acids, acid halides, aldehydes, etc. The activity of the methylene bases is determined by their structure, in which the most important role belongs to the bipolar structure:



A great part of the reactions of methylene bases, at least in the first phase, may be represented as addition according to the mechanism.

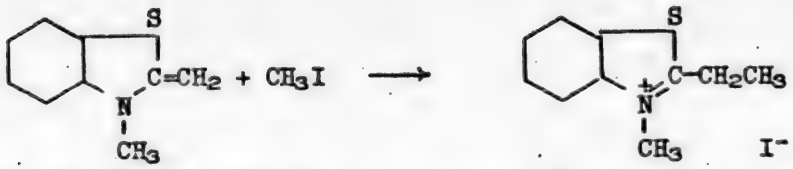


It appeared to us that the reaction of methylene bases with alkyl halides deserved special attention. If it proceeds in the manner indicated above, it should result in the lengthening of the side chain of the methylene bases. In this case, we should have a method of synthesis that would permit us to obtain new methylene bases and quaternary salts, of value as intermediates in the synthesis of cyanine dyes and various physiologically active compounds.

It is known that methylene bases of the indolenine series, in fact, react in just this way [1]. In the same way, the methylene bases from the ester of lutidinedicarboxylic acid [2] react with methyl iodide and dimethylsulfate, and the methylene bases from quinaldine [3] react with benzyl iodide. But with regard to the reactions of methylene bases of the thiazole series with alkyl halides, the literature contains nothing at all.

Our preliminary experiments showed that 3-methyl-2-methylenebenzothiazoline reacts with methyl iodide with the evolution of heat and the formation of a mass of yellow crystals.

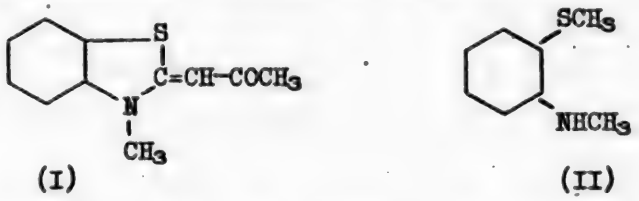
In view of what has been said above, we supposed that the product of this reaction would be the methyl iodide of the 2-ethylbenzothiazole:



Contrary to what we had expected, we obtained a completely different compound. Analysis of the product of methylation showed that with one mole of methyl iodide there united not one mole of the methylene bases, as had taken place in the previous cases, but two moles. The product of methylation appeared as a yellow, crystalline substance, insoluble in benzene and ether, slightly soluble in water, easily soluble in hot alcohol and chloroform. Under the action of diluted hydrochloric acid or alkali, it is easily hydrolyzed to give two new compounds. If hydrolysis was carried out in the presence of alkali, a solid substance with m.p. 160-161° was formed, along with a liquid of basic character, with b.p. 127-128° at 11-12 mm. In the presence of hydrochloric acid, the hydrochlorides of these compounds were obtained.

An investigation of the compound with m.p. 160-161° showed that it was identical with 3-methyl-2-acetylmethylenebenzothiazoline (I), first obtained by the Kodak Company [4] by the action of acetyl chloride upon the methyl iodide of 2-methylbenzothiazole in pyridine. A mixed test for melting point with the compound synthesized according to the method of the Kodak patent gave no depression.

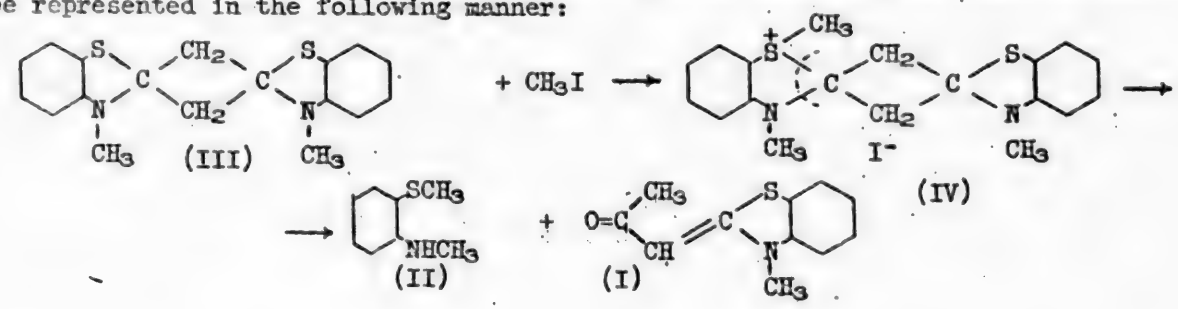
The liquid substance appeared to be o-methylmercapto-N-methylaniline (II):



(I) (II)

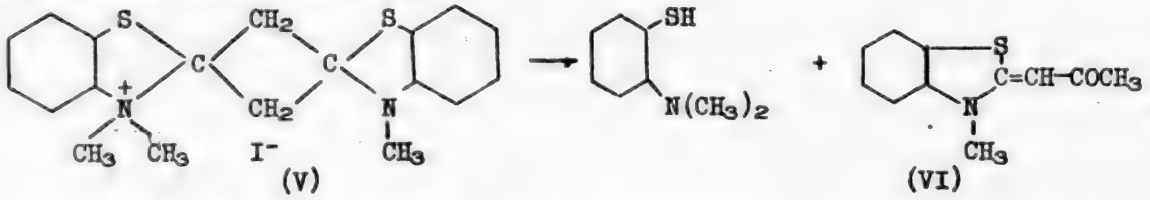
It dissolved in acids, but not in alkalies, and could be acetylated and nitrosated. The nature of the compound was conclusively determined by its synthesis. N-methyl--o-aminothiophenol, obtained from the methylmethosulfate of 2-methylbenzothiazole by the action of alcoholic alkali [5], was methylated with dimethyl sulfate in alkaline solution. The product appeared identical with the liquid compound which is of interest to us. The acetyl derivatives of both compounds, both alone and in mixed tests, all melted at 81-82°.

We considered the peculiar course of the reaction between methyl iodide and the methylene bases from 2-methylbenzothiazole in connection with the circumstance that this methylene base, as Mumm and his coworkers showed, exists in the form of a dimer. It dimerizes completely in benzene solution. As one mole of methyl iodide combines with two moles of the base, it was natural to assume that it was the dimer molecules which took part in the reaction. The mechanism of the reaction could then be represented in the following manner:



The methyl iodide and the dimer of the methylene bases (III) form a thionene salt (IV). This salt hydrolyzes with the cleavage of one of the thiazole rings.

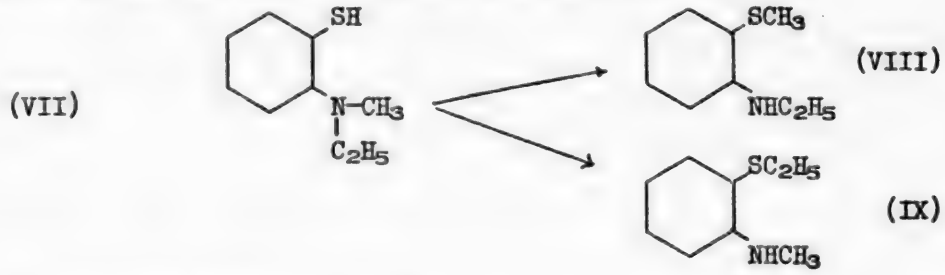
It appeared to us at first, however, improbable that the formation of the salt should take place upon the sulfur atom, and not upon the nitrogen. We did not exclude the possibility that methylation might take place on the nitrogen atom with the formation of compound (V), and that its hydrolysis might give N,N-dimethyl-o-aminophenylmercaptan (VI):



(V) (VI)

and that this might then isomerize to give o-methylmercapto-N-methylaniline (II).

Later, we were able to show that this kind of isomerization does not take place, and that the reaction does not take this course. In fact, if it did take place in this way, 3-methyl-2-methylenebenzothiazoline and ethyl iodide should have given N-methyl-N-ethyl-o-aminophenylmercaptan (VII), and as a result of the isomerization of the latter, a mixture of the two bases: o-methylmercapto-N-ethylaniline (VIII) and o-ethylmercapto-N-methylaniline (IX):

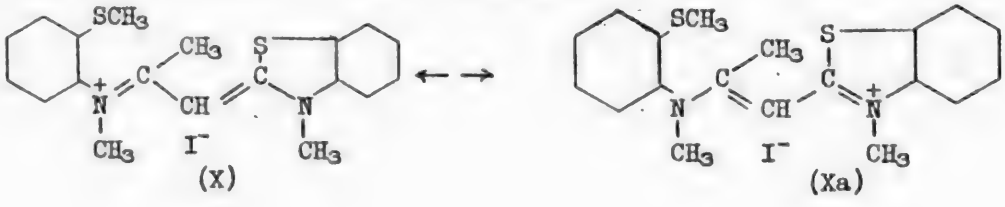


(VII) (VIII) (IX)

The reaction of 3-methyl-2-methylenebenzothiazoline with ethyl iodide was investigated, and among the products of hydrolysis of the compound obtained, only o-ethylmercapto-N-methylaniline (IX) was found. Consequently, no jumping over of the radicals takes place.

Thus, we may consider it as proved that in the action of alkyl iodides upon methylene bases of the benzothiazole series, the alkyl is at once attached to the sulfur atom. We cannot, however, conclude from this that the compound obtained has the structure corresponding to formula (IV).

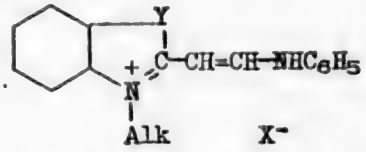
Although formula (IV) also permits us to explain the formation of the products of hydrolysis, it remains unclear why the initial addition product of the alkyl iodide is colored, and why the reaction for the formation of this compound takes place so easily if it has an unstable four-membered ring. It would appear far more probable that at the moment of reaction with alkyl iodide a rupture of the thiazole ring would take place to give compound (X):



(X) (Xa)

Compound (X) would have to be colored because of the resonance of the ionic structures (X) and (Xa). It would have a tendency to hydrolytic cleavage, inasmuch as it is a derivative of the anil of 3-alkyl-2-acetylmethylenebenzothiazoline.

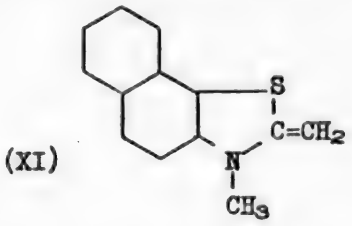
Substances similar to our addition products with alkyl iodides are known. They are obtained in the form of acetyl derivatives by the reaction of quaternary salts of nitrogen heterocycles which contain active groups with diphenylformamidines in acetic anhydride [7]. Their structure corresponds to the general formula:



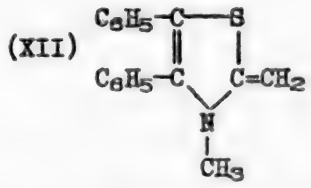
Like our products, they are colored yellow, and are hydrolyzed [8] upon heating in aqueous alcoholic solution in the presence of acid or alkali. With quaternary salts of nitrogen heterocycles in the presence of bases, the acetyl derivatives of these compounds form cyanine dyes. The products of the alkylation of methylene bases, obtained by us, upon heating with quaternary salts in pyridine form only traces of dyes.

Having explained the structure of the reaction products of methyl and ethyl iodide with the methylene bases from 2-methylbenzothiazole, we attempted to show to what degree the alkylation mechanism we had found could be considered general for the other methylene bases of the thiazole series.

For this purpose we obtained methylene bases not described in the literature, from 2-methyl-α-naphthothiazole (XI) and from 2-methyl-4,5-diphenylthiazole (XII):



(XI)

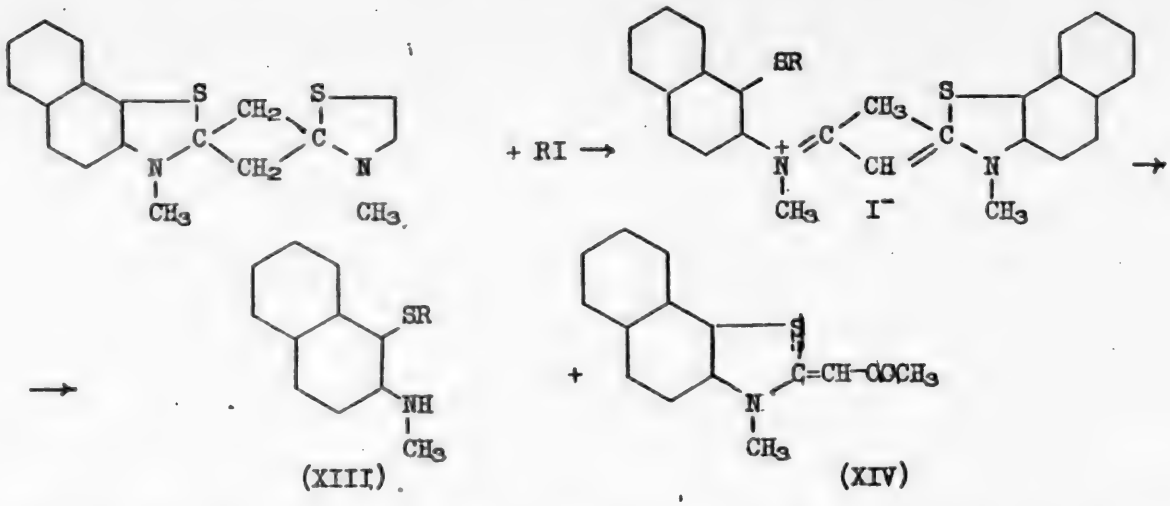


(XII)

and investigated the reactions of these bases with methyl and ethyl iodides. The 2-methyl-4,5-diphenylthiazole was chosen because it gives a crystalline methylene base. The quaternary salts of other, simpler derivatives of thiazole, upon treatment with alkalies, did not give crystalline methylene bases.

The action of methyl iodide on 3-methyl-2-methylene-α-naphthothiazoline gives a yellow crystalline substance, insoluble in the usual solvents. The reaction takes place less energetically than with 3-methyl-2-methylenebenzothiazoline, but still fairly easily. The methylation product is completely insoluble in water, and therefore hydrolyzes in aqueous medium very slowly; however, upon heating with aqueous alcohol in the presence of acids or alkalies, hydrolysis is completed in a few minutes. The reaction of 3-methyl-2-methylene-α-naphthothiazoline with ethyl iodide gives a yellow crystalline substance, whose properties are similar to those of the product of methylation.

In connection with what has been said above, we believe that the reaction of 3-methyl-2-methylene-α-naphthothiazoline with alkyl halides and the hydrolysis of the products thus formed take place in the following manner:

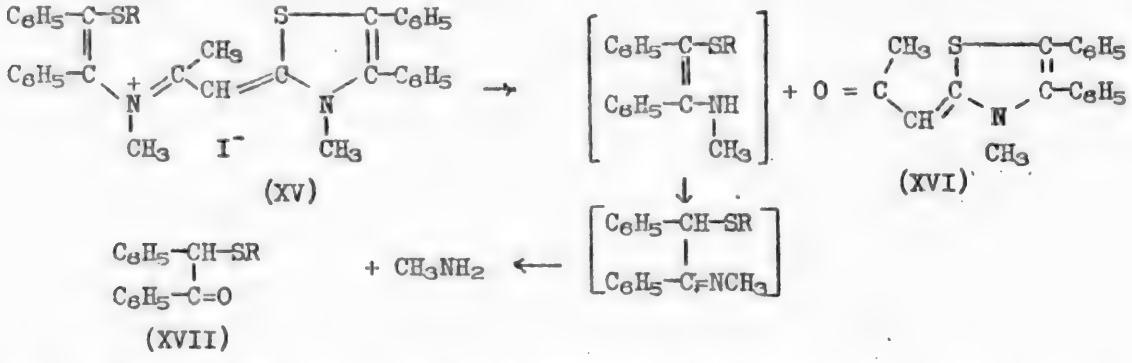


(XIII) (XIV)

In agreement with this mechanism, both products obtained by us gave one and the same substance upon hydrolysis, with m.p. 202-203°. This substance was 3-methyl--2-acetylmethylene-α-naphthothiazoline (XIV). It was insoluble in alkali, and formed a salt with hydrochloric acid, stable only in the presence of an excess of acid; with quaternary salts of nitrogen heterocycles containing active methyl groups, it formed dyes. Compound (XIV) is known, and its melting point is given in the literature as 201-203° [8].

In addition to 3-methyl-2-acetylmethylene-α-naphthothiazoline, hydrolysis of the addition product of methyl iodide gave a crystalline compound with m.p. 55°; hydrolysis of the addition product of ethyl iodide gave a colorless liquid, with b.p. 190° at 7 mm. On the basis of the analyses, the ability to dissolve in acids, the ability to be acetylated and nitrosated, and finally, on the basis of the method of formation, we consider that these compounds are 1-methylmercapto-2-methylaminonaphthalene (XIII, R = CH_3) and 1-ethylmercapto-2-methylaminonaphthalene (XIII, R = C_2H_5), respectively.

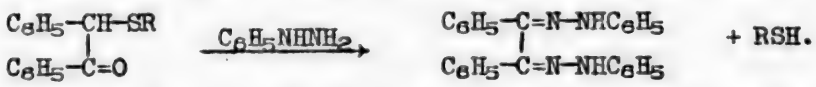
3-Methyl-4,5-diphenyl-2-methylenethiazoline (XII) reacts very easily with methyl and ethyl iodides. In both cases, yellow crystalline addition products (XV) are obtained. They are easily hydrolyzed by aqueous solutions of acids and alkalies. As here we have a mononuclear methylene base, hydrolysis takes place somewhat differently than in the preceding cases.



(XV) (XVI) (XVII)

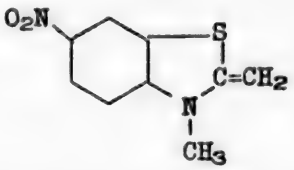
The first product of hydrolysis is 3-methyl-4,5-diphenyl-2-acetylmethylenethiazoline (XVI), almost colorless crystals with m.p. 229-230°. The properties of this substance are similar to the properties of the other acylmethylene bases already described.

In addition to the acylmethylene bases, hydrolysis gives methylamine and desylalkylsulfide. From the methylation products, desylmethylsulfide (XVII, R = CH_3) can be isolated as large needles with m.p. 75-76°, and from the products of ethylation, desylethylsulfide (XVII, R = C_2H_5) needles with m.p. 78°. The structure of these compounds can be derived chiefly on the basis of the method of preparation and of the analytical data. We endeavored, in addition, to obtain phenylhydrazones of these compounds. With this purpose in mind, equimolecular quantities of desalkylsulfide and phenylhydrazine were heated for a short time at 50-60° in glacial acetic acid. In both cases, a precipitate was formed; after recrystallization from chloroform, these precipitates were in the form of faintly yellowish needles with m.p. 225-226°. The compound with m.p. 225-226° seemed identical with the bisphenylhydrazone of benzil. Its formation may be indicated as follows:



During the heating of the components in glacial acetic acid, a very strong mercaptan odor was noted.

We obtained 3-methyl-6-nitro-2-methylenebenzothiazoline



upon heating this with methyl iodide or dimethyl sulfate, no addition products were formed. Upon heating for a short time, the methylene bases remain unchanged; upon continued heating, the mixture contained in addition to the methylene bases the methyl iodide or the corresponding methylmethosulfate of 2-methyl-6-nitrobenzothiazole.

EXPERIMENTAL

The Reaction of 3-Methyl-2-methylenebenzothiazoline with Methyl Iodide

3-Methyl-2-methylenebenzothiazoline was obtained by the method of Mumm, Hinz, and Diederichsen [6].

22 g of freshly prepared base with m.p. 164-166° was dissolved in 50 ml of chloroform, and 20 g (1 mole) of methyl iodide was added to the solution. The reaction began in the cold and proceeded with the evolution of heat. After 2 to 3 minutes, the mixture was converted into a thick gruel of fine yellow needles. After standing for 10 minutes, the reaction product was filtered off, washed with 50 ml of chloroform, and dried. Yield 30 g, or 95% of theory. After recrystallization from chloroform, the substance was in the form of yellow needles with m.p. 229-230° (temperatures here and later are corrected). The same substance was formed by the action of methyl iodide on the methylene bases in benzene, ether, nitrobenzene, acetone, and alcohol. In the last case, a very impure product was obtained, as the methylene bases, even upon heating with alcohol for only a short period, acquired an intense red color.

Found %: N 5.76; I 26.83.
$C_{19}H_{21}N_2S_2I$. Calculated %: N 5.98; I 27.10.

31 g of the addition product, 100 ml of water, and 10 ml of concentrated hydrochloric acid were heated to boiling for 10 minutes. As a result of hydrolysis, the slightly water-soluble substance went completely into solution. Upon cooling, long needles of the hydrochloride of 3-methyl-2-acetylmethylenebenzothiazoline (I)

crystallized from the solution. These were filtered off, washed with water, and converted by the action of a solution of caustic potash into 3-methyl-2-acetylmethylenebenzothiazoline. The yield of the latter was 13 g, or 96% of theory, m.p. 157-158°. The substance crystallized from alcohol or from water in the form of long needles containing one molecule of water of crystallization. Upon drying in a vacuum dessicator above calcium chloride, the water was given off, and the needles turned into powder. M.p. 160-161°. A mixed test with the same compound, obtained by the action of acetyl chloride upon the methyl iodide of 2-methylbenzothiazole in pyridine, according to the Kodak patent (m.p. 160°) gave no depression.

Found %: N 6.25, 6.18.
$C_{11}H_{11}ONS \cdot H_2O$. Calculated %: N 6.28.

After the separation of the hydrochloride of 3-methyl-2-acetylmethylenebenzothiazoline, caustic soda was added to the mother liquor until the reaction was alkaline; the oil which settled to the bottom of the beaker was extracted with ether. The o-methylmercapto-N-methylaniline was dried over potash and distilled in vacuum. B.p. 126-128° at 11-12 mm, yield 9 g, or 87% of theory.

The o-methylmercapto-N-methylaniline was insoluble in water, very soluble in ether, benzene, chloroform, and alcohol. It was unchanged by the action of alkali, and formed salts with acids. The hydroiodide was in the form of crystals with m.p. 164°, almost insoluble in water.

Found %: N 4.95.
$C_8H_{12}NSI$. Calculated %: N 4.98.

The acetyl derivative was obtained by the action of acetyl chloride upon the benzene solution of the base. After recrystallization from water, the m.p. was 81-82°. The compound was identical with the product of acetylation of o-methylmercapto-N-methylaniline, obtained from N-methyl-o-aminothiophenol.

The Reaction of 3-Methyl-2-methylenebenzothiazoline with Ethyl Iodide

In a flask with a reflux condenser, 12.5 g of methylene bases, 35 ml of chloroform, and 6 g of ethyl iodide were heated on the water bath at the boiling point for 5 minutes. The mixtures acquired an intense yellow-orange color. The chloroform was driven off, and benzene was added to the oily residue. A yellow crystalline mass was formed. The crystals were filtered off and washed with benzene. Yield 17.7 g, or 96% of theory. Melting point after recrystallization from acetone, 190-191°.

Found %: I 26.03.
$C_{20}H_{23}N_2S_2I$. Calculated %: I 26.32.

A mixture of 15 g of the addition product of ethyl iodide and 3-methyl-2-methylenebenzothiazoline, 8 ml of concentrated hydrochloric acid, and 50 ml of water was heated on the boiling water bath for 5 minutes. After cooling, the hydrochloride of 3-methyl-2-acetylmethylenebenzothiazoline was filtered off. From it, as in the preceding case, there was obtained the free 3-methyl-2-acetylmethylenebenzothiazoline. Yield 5.8 g, or 91% of theory; the melting point after recrystallization from alcohol was 159-160°.

After separation of the hydrochloride of the acetylmethylene base, the mother liquor was treated with alkali, and the oil which settled out was extracted with ether. After drying over potash and removal of the ether, there was obtained 4 g of liquid product which was almost pure o-ethylmercapto-N-methylaniline (IX). Distillation in vacuum (112-114° at 2 mm) gave 3.8 g or 73% of theory. The properties of this compound were similar to the properties of the o-methylmercapto-N-methylaniline described above. The action of acetyl chloride gave the acetyl derivative; after recrystallization from petroleum ether, this was in the form of colorless

plates with m.p. 55°. A mixed test for the melting point of this substance with the product of acetylation of o-ethylmercapto-N-methylaniline obtained from N-methyl-o-aminothiophenol gave no depression.

The Reaction of 3-Ethyl-2-methylenebenzothiazoline with Methyl Iodide

To the benzene solution of 4 g of 3-ethyl-2-methylenebenzothiazoline, 3.2 g of methyl iodide was added. The reaction began in the cold. To complete the reaction, the mixture was heated several minutes at 60°. The crystals formed were filtered off and washed with benzene. Yield, 5.15 g, or 92% of theory. Upon recrystallization from alcohol, the compound was in the form of yellow needles, melting with decomposition at 192-193°.

Found %: N 5.54; I 25.99, 25.93.
$C_{20}H_{23}N_2S_2I$. Calculated %: N 5.81; I 26.32.

5 g of the addition product was heated on the water bath with 5 ml of concentrated hydrochloric acid and 30 ml of water for several minutes. Upon cooling, the hydrochloride of 3-ethyl-2-acetylmethylenebenzothiazoline crystallized out. From this salt, the action of alkali gave the acetylmethylene base with a yield of 1.9 g, or 83% of theory; m.p. 115-116°. According to the literature, the melting point of 3-ethyl-2-acetylmethylenebenzothiazoline is 116-117°.

Found %: N 6.47.
$C_{12}H_{13}ONS$. Calculated %: N 6.39.

The addition of alkali to the mother liquor caused the separation of o-methylmercapto-N-ethylaniline (VIII) in the form of a colorless oil with b.p. 99-101° at 2-3 mm. The acetyl derivative was in the form of colorless crystals with m.p. 66-67°. A mixed test of this compound and the acetyl derivative of o-ethylmercapto-N-methylaniline (m.p. 55°) melted at 42-50°.

Found %: N 6.78.
$C_{11}H_{15}ONS$. Calculated %: N 6.70.

The Reaction of 3-Methyl-2-methylene-α-naphthothiazoline with Methyl Iodide

3-Methyl-2-methylene-α-naphthothiazoline (XI) was obtained from the quaternary salt of 2-methyl-α-naphthothiazole by the action of alkali. In a separatory funnel, 2.1 g of solid caustic potash in 150 ml of acetone and 15 ml of water were added to 8.4 g of the methylmethosulfate of 2-methyl-α-naphthothiazole. The mixture was shaken for a few minutes; 4.1 g (74% of theory) of the methylene bases precipitated out as small light yellow plates insoluble in water and alcohol, almost insoluble in acetone, and slightly soluble in cold benzene. The compound dissolved well in chloroform and in dichloroethane to give a yellow color, and in nitrobenzene to give a red color. M.p. 200-203°, with decomposition.

Found %: N 6.35.
$C_{13}H_{11}NS$. Calculated %: N 6.57.

The molecular weight of the compound was determined by the cryoscopic method in nitrobenzene. The determination showed that the compound formed the dimer to a considerable extent.

Found: M 305, 316.
$C_{13}H_{11}NS$. Calculated: M 213.

In a flask with a reflux condenser, 4.9 g (1 mole) of methyl iodide was added to a suspension of 7.4 g of the methylene base in 20 ml of dichloroethane. The mixture was heated at 70-80° for several minutes. At the bottom of the flask, yellow, fairly large crystals settled out. The yield of addition product was 9.6 g, or 97% of theory. The melting point before recrystallization was 274-275°, after recrystal-

lization from pyridine, 276-277°. The compound was insoluble in water, alcohol, benzene, ether, and dichloroethane, slightly soluble in glacial acetic acid, chloroform, and pyridine.

Found %: I 22.43, 22.57.
$C_{27}H_{25}N_2S_2I$. Calculated %: I 22.33.

To 10 g of unrecrystallized material with m.p. 274-275° there was added 50 ml of alcohol and a solution of 0.9 g of caustic soda in 5 ml of water. The mixture was heated to boiling for 5 minutes. The precipitate went into solution as a result of hydrolysis. Upon cooling, 3-methyl-2-acetylmethylene-α-naphthothiazoline crystallized out; after recrystallization from alcohol, the amount obtained was 2.65 g, with m.p. 202-203° (according to the literature [9], the m.p. is 201-203°).

The alcoholic mother liquor was concentrated, and the oily precipitate extracted with ether. From the substance which was insoluble in ether, after purification by crystallization from alcohol, an additional 0.9 g of the acetylmethylene base was obtained, giving a total yield of 3.55 g, or 79% of theory.

From the ether extract, after drying and removal of the ether, there was obtained 3.4 g, or 96% of theory, of 1-methylmercapto-2-methylaminonaphthalene (XIII, R = CH_3) in the form of a faintly yellow oil, which crystallized on standing. After crystallization from alcohol, m.p. 55°.

Found %: N 6.97.
$C_{12}H_{13}NS$. Calculated %: N 6.89.

The acetyl derivative of 1-methylmercapto-2-methylaminonapththalene was obtained by prolonged heating with acetic anhydride. The melting point after crystallization from alcohol was 127°.

Found %: N 5.78.
$C_{14}H_{15}ONS$. Calculated %: N 5.71.

The Reaction of 3-Methyl-2-methylene-α-naphthothiazoline with Ethyl Iodide

A mixture of 6.8 g of the methylene base, 7.5 g (3 moles) of ethyl iodide and 15 ml of benzene was heated on a water bath for 1 hour. The yield of yellow-green crystals was 8.6 g, or 92% of theory. M.p. 246-247°, with decomposition. The substance was insoluble in the usual solvents.

Found %: I 21.36.
$C_{28}H_{27}N_2S_2I$. Calculated %: I 21.79.

Hydrolysis of the addition product took place on brief heating with an alcoholic solution of caustic soda. The solution was treated with animal charcoal. Upon cooling, 3-methyl-2-acetylmethylene-α-naphthothiazoline crystallized out. Yield 2 g; m.p. 199-201°. A mixed test with the acetylmethylene base previously obtained (m.p. 202-203°) gave no depression.

The addition of water to the alcoholic filtrate precipitated a red-brown oil, consisting of 1-ethylmercapto-2-methylaminonaphthalene (XIII, R = C_2H_5), with an admixture of the acetylmethylene base. The 1-Ethylmercapto-2-methylaminonaphthalene was extracted with ether and distilled in vacuum. Yield 1.35 g, or 52% of theory. B.p. 190° at 7 mm. Upon heating with acetic anhydride, the acetyl derivative was obtained. After recrystallization from petroleum ether, this had m.p. 112-113°.

Found %: N 5.65.
$C_{15}H_{17}ONS$. Calculated %: N 5.40.

The Reaction of 3-Methyl-4,5-diphenyl-2-methylenethiazoline with Methyl Iodide

3-Methyl-4,5-diphenyl-2-methylenethiazoline (XII) was obtained from the methylmethosulfate of 2-methyl-4,5-diphenylthiazole by the same method as the

preceding methylene bases. Yield 91% of theory; small yellow plates with m.p. 152-154°, with decomposition. The compound was insoluble in water, almost insoluble in alcohol, easily soluble in benzene with a pale yellow color, in chloroform with an orange-red color, and in nitrobenzene with a red color.

Found %: N 5.42.
$C_{17}H_{15}NS$. Calculated %: N 5.28.

The molecular weight was determined in benzene:

Found %: M 431, 462.
$C_{17}H_{15}NS$. Calculated %: M 265.

The reaction of the methylene base with methyl iodide took place in benzene solution in the cold with marked evolution of heat. The yield of addition product with methyl iodide was quantitative. After recrystallization from alcohol, yellow crystals were obtained; m.p. 183-184°, with decomposition.

Found %: S 9.23.
$C_{35}H_{33}N_2S_2I$. Calculated %: S 9.54.

4.5 g of the addition product, 10 ml of alcohol, and 3 ml of concentrated hydrochloric acid were heated for several minutes on a water bath. Upon cooling, desylmethylsulfide (XVII, R = CH_3) crystallized out in the form of large, colorless needles. Yield of desylmethylsulfide 1.6 g; after recrystallization from alcohol, 1 g. M.p. 75-76°.

Found %: S 13.52, 13.23.
$C_{15}H_{14}OS$. Calculated %: S 13.24.

In order to obtain the phenylhydrazone, 0.5 g of desylmethylsulfide and 0.3 g of phenylhydrazine in 2 ml of glacial acetic acid were heated on the water bath for 1 hour, and allowed to stand over night. A quantity of 0.12 g of the crystalline hydrazone was obtained. After recrystallization from chloroform, a faintly yellowish substance was obtained, which contained no sulfur; m.p. 225-226°. It appeared identical with the bisphenylhydrazine of benzil. Upon heating the reaction mixture, a strong odor of mercaptan was noted.

The filtrate from the desylmethylsulfide, containing the salt of the acetylmethylene base (XVII) and methylamine hydrochloride, was treated with caustic potash. The methylamine was driven off and identified in the form of the hydrochloride (m.p. 225-226°). After the removal of the methylamine, the residue gave 3-methyl-4,5-diphenyl-2-acetylmethylenethiazoline in a yield 80% of theory. The melting point after recrystallization from alcohol was 229-230°. It was insoluble in water, slightly soluble in ether and acetone, slightly more soluble in benzene.

Found %: N 4.59.
$C_{19}H_{17}ONS$. Calculated %: N 4.56.

Upon heating with the quaternary salts of nitrogen heterocycles containing an active methyl group, the compound easily formed cyanine dyes.

The Reaction of 3-Methyl-4,5-diphenyl-2-methylenethiazoline with Ethyl Iodide

From 4 g of the methylene base and 2.34 g of ethyl iodide in 20 ml of benzene, the method of the previous section gave. 4.8 g, or 93% of theory, of a yellow crystalline substance with m.p. 214-215°, with decompositon.

Found %: I 18.25.
$C_{36}H_{35}N_2S_2I$. Calculated %: I 18.49.

Hydrolysis, carried out in the presence of hydrochloric acid in alcohol solution, gave 75% of theory of 3-methyl-4,5-diphenyl-2-acetylmethylenethiazoline, with m.p.

229-230°, and 83% of theory of desylethylsulfide (XVII, R = C_2H_5); with m.p. 78°.

Found %: S 12.84.
$C_{16}H_{16}OS$. Calculated %: S 12.52.

Phenylhydrazine gave with desylethylsulfide the same bisphenylhydrazone of benzil, with m.p. 225-226°.

The Reaction of 3-Methyl-6-nitro-2-methylenebenzothiazoline with Methyl Iodide

3-Methyl-6-nitro-2-methylenebenzothiazoline (XVIII) was obtained by the same method as the previous methylene bases. From 5 g of the methyl methosulfate of 2-methyl-6-nitrobenzothiazole there was obtained 2.4 g, or 75% of theory, of the methylene base, in the form of orange-red crystals with m.p. 230-232°, with decomposition.

Found %: N 13.50.
$C_9H_8O_2N_2S$. Calculated %: N 13.51.

The determination of the molecular weight in nitrobenzene showed that this methylene base also formed a dimer.

Found: M 367, 348.
$C_9H_8O_2N_2S$. Calculated: M 208.

1 g of the methylene base was heated in a sealed tube with 2 g of methyl iodide at 100° for 3.5 hours. After evaporation of the methyl iodide, the residue was dissolved in hydrochloric acid, and treated with potassium iodide. This gave the methyliodide of 2-methyl-6-nitrobenzothiazole.

In a second experiment, 0.3 g of the methylene bases was heated with 0.3 g of dimethyl sulfate in chloroform solution for 1 hour at 130°. From the products it was possible to separate only the methylmethosulfate of 2-methyl-6-nitrobenzothiazole, with m.p. 203-204°.

SUMMARY

The reactions between alkyl iodides and methylene bases of the thiazole series have been investigated. It has been shown that these bases form with great ease yellow crystalline addition products containing one mole of alkyl iodide to two moles of the methylene bases. Addition products of methyl and ethyl iodide have been obtained with 3-methyl-2-methylenebenzothiazoline, 3-methyl-2-methylene-α-naphthothiazoline, 3-methyl-4,5-diphenyl-2-methylenethiazoline, and also the addition product of methyl iodide with 3-ethyl-2-methylenebenzothiazoline. The structures of these compounds have been determined.

In the presence of acids and alkalies, these compounds are easily hydrolyzed. Upon hydrolysis, the addition products of alkyl iodides and 3-methyl-2-methylenebenzothiazoline give 3-methyl-2-acetylmethylenebenzothiazoline and o-alkylmercapto-N-methylaniline. Similarly, the addition products of alkyl iodides and 3-methyl-2-methylene-α-naphthothiazoline give 3-methyl-2-acetylmethylene-α-naphthothiazoline and 1-alkylmercapto-2-methylaminonaphthalene. Hydrolysis of the addition products of alkyl iodides and 3-methyl-4,5-diphenylthiazoline gives 3-methyl-4,5-diphenyl-2-acetylmethylenethiazoline, desylalkylsulfide, and methylamine.

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INVESTIGATIONS IN THE FIELD OF HYDROXYFUCHSONE DYES

X. THE SO-CALLED TAUTOMERISM OF HYDROXYTRIARYLCARBINOLS

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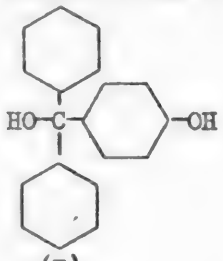
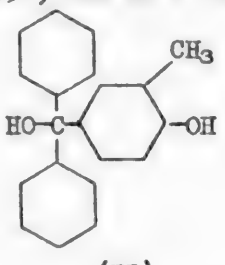
It was long ago observed that hydroxytriarylcarbinols, depending on the conditions of their isolation or crystallization, could be obtained either in colorless form, or with a yellow color; as a rule, the colored modification of any given hydroxytriarylcarbinol melted lower than the colorless form. These properties of hydroxytriarylcarbinols were first observed at the beginning of the present century in the original member of the series, 4-hydroxytriphenylcarbinol (I). In 1901, Bistrzhitsky and Herbst [1] obtained this substance, after crystallization from 50% acetic acid, in the form of yellow crystals with a constant m.p. 138-139°; however, Auwers and Schroetter [2] soon showed that if these colored crystals were dissolved in alkali and carbon dioxide gas was passed through the colorless solution thus obtained, then hydroxytriphenylcarbinol separated in the colorless form, with m.p., after crystallization from benzene, of 157-159°. Upon careful crystallization, the melting point could rise, in certain cases, to 165°.

Somewhat later, in 1903, Bistrzhitsky and Zurbriggen [3] observed that 3-methyl-4-hydroxytriphenylcarbinol (II) also could be isolated in two modifications, colorless and colored. Ten years later, Gomberg [4], who became interested in 4-hydroxytriphenylcarbinol in connection with his investigations in the field of triphenylmethyl, obtained, together with his coworkers [5,6] a series of derivatives of this substance which contained different substituents in the ortho position to the hydroxyl group. All these derivatives of 4-hydroxytriphenylcarbinol could be isolated either in a colored or a colorless form. As an example, we may take 3-methoxy-4-hydroxytriphenylcarbinol (III), which was obtained in a colorless modification with m.p. 159°, and in a colored modification with m.p. 146-147°.



(I)



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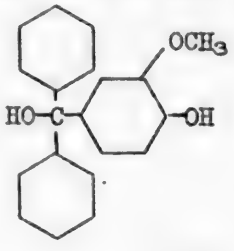


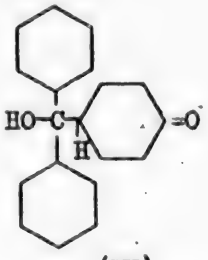
(III)

Already, by 1932, Bistrzhitsky and Yablonsky [7] had investigated derivatives of 4-hydroxytriphenylcarbinol containing substituents, in particular methoxy groups, as well as other nuclei of the triarylmethane classification, and had observed that these substances too could be obtained either in colorless or in colored form.

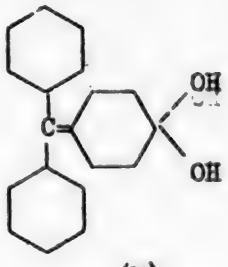
A study of the properties of the colorless and colored modifications of the hydroxytriarylcarbinols revealed that they had exactly the same elementary composition, and could be converted into each other. Upon moderate heating of the colorless

hydroxytriarylcarbinol, it turned yellow, and its melting point was lowered, approaching that of the colored modification; by the crystallization of the colorless hydroxytriarylcarbinols from 50-70% acetic acid, the yellow, low-melting modifications were obtained. On the other hand, by the crystallization of both the colorless and the colored modifications of the hydroxytriarylcarbinols from alcohol containing ammonia, or from benzene to which pyridine had been added, the colorless hydroxytriarylcarbinols were obtained. Both modifications dissolved in aqueous alkalies to give colorless solutions. These same solutions were obtained by treatment with alkali of the fuchsones with corresponding structures. From these colorless alkaline solutions, the hydroxytriarylcarbinols could be separated either in a colored or in colorless form: upon acidification of the alkaline solution with acetic acid, the yellow modification precipitated; upon the passage of carbon dioxide through the alkaline solution, or still better, upon the addition of ammonium chloride, the colorless hydroxytriarylcarbinol precipitated out. But in the latter case, even during the filtration, the precipitate usually acquired a yellow color.

On the basis of these properties of the hydroxytriarylcarbinols, there developed the opinion that the colorless and colored modifications were tautomers, or, more accurately, desmotropes. The first suggestion concerning the tautomerism of the hydroxytriarylcarbinols was expressed back in 1903, by Bistrzhitsky and Herbst [8]. They considered that the colorless hydroxytriphenylcarbinol had the structure (I); to the colored tautomer, they ascribed the quinoid-like structure (IV). This form, which was the first to be isolated, they at first called α-hydroxytriphenylcarbinol; later, Bistrzhitsky and Yablonsky [7] proposed for it the name pseudohydroxytriphenylcarbinol.



(IV)



(V)

The idea of the tautomerism of the hydroxytriarylcarbinols was supported by Gomberg [4], who saw in this a confirmation of his views on the structure of the triarylmethyls and the triarylmethane dyes. Gomberg's school studied this question and devoted a series of investigations to it; several of these [8,9,10] were even published under the title On the Tautomerism of the Hydroxytriarylcarbinols. But Gomberg differed from Bistrzhitsky in proposing for the colored desmotrope of 4-hydroxytriphenylcarbinol not the carbinol, but the quinol structure (V), and he decided that the colored desmotropes of the other hydroxytriarylcarbinols had a similar structure. All the same, Bistrzhitsky and Yablonsky [7], returning in 1932, after a lengthy interruption, to investigations in this field, cited Gomberg's formula without critical consideration, and themselves continued to ascribe to the pseudo-hydroxytriarylcarbinols and to the colored desmotropes of other hydroxy triarylcarbinols the structure (IV).

However, the dispute about the structure of pseudo-hydroxytriarylcarbinols seemed to us pointless; on the basis of our investigations, we arrived at the conclusion that the desmotropism of the hydroxytriarylcarbinols described above was more than doubtful.

Gomberg, the most consistent defender of the position that the hydroxytriarylcarbinols were desmotropes, saw what appeared to him a completely satisfactory

confirmation of his opinion in the fact that the colored forms of the hydroxytriarylcarbinols, upon crystallization from acetic acid, had melting points and other properties which did not change upon repeated crystallization. In addition, he considered that a comparison of the behavior of the colorless and the colored modifications upon heating, and a comparison of the absorption curves for light in the ultraviolet part of the spectrum confirmed his opinions.

Even during his first investigation of hydroxytriphenylcarbinol, Gomberg [4] noted that the colorless form split off water with more difficulty than did the colored form in its transformation into fuchsone. Thus, for example, upon heating at 100° for 30 minutes, the colored form gave 50% of the theoretically calculated amount of water, the colorless form gave only 10%. However, later, Gomberg and van Stone [6] noted that the conversion of hydroxytriarylcarbinols into fuchsones at high temperatures was accompanied by side reactions of decomposition; therefore, they proceeded to compare the velocities of dehydration of what were in their opinion tautomeric forms of hydroxytriarylcarbinols by heating at 75°. For this purpose, accurately weighed samples of the 'desmotropes' to be compared were placed in small porcelain boats, heated in a copper tube, which was placed in a copper glycerine bath, while a stream of dry air was passed through the tube and over the surface of the compounds. Upon the expiration of a definite period of time, the boats were weighed, and thus the loss in weight of the substances under investigation was found.

According to the data of Gomberg and van Stone, under these conditions, the colored 'desmotropes' showed a loss in weight which corresponded to the calculated theoretical value for the conversion of the hydroxytriarylcarbinols into the corresponding fuchsones much more rapidly than did the colorless forms. Most significant were the results they obtained by this sort of comparison of the colorless and colored forms for 3-methoxy-4-hydroxytriphenylcarbinol (III); in the colored form, the loss in weight corresponding to the theoretical value calculated for the loss of 1 mole of water was reached in 2 hours, 15 minutes, while the colorless form attained this same point only in 156 hours.

These results, in the opinion of Gomberg and van Stone, were one of the most satisfactory confirmations not only of the desmotropy of the hydroxytriarylcarbinols, but also of the quinol structure (V) of the colored 'desmotropes'. The presence in the latter of two hydroxyl groups on one and the same carbon atom supposedly resulted in the relatively rapid splitting off of water, in comparison with the colorless form, to give fuchsone; the colorless, more stable hydroxytriarylcarbinols, in Gomberg's opinion, upon heating first isomerized to give the colored 'desmotropes', which as they were formed, gave off water, and were converted into fuchsones.

We decided to carry out an accurate reproduction of these experiments of Gomberg and van Stone; as the compound to be investigated, we chose 3-methoxy-4-hydroxytriphenylcarbinol, which gave, in the experiments of Gomberg and van Stone, the most significant results; this could be obtained by a method described by us in detail in a previous communication [11]. However, wishing to observe carefully everything that happened in the process, we carried out our experiments not in copper, but in glass apparatus.

Definite samples of the finely powdered colorless and colored forms of the substance had melting points 159° and 146-147° respectively; this corresponded accurately to the figures given by Gomberg and van Stone. We weighed the samples in small porcelain boats, and heated them at 75° (with an accuracy of $\pm$ 1°), in a glass tube, placed in a glass glycerine bath, while a steady stream of dried air was passed through the tube. The exit end of the tube was fitted with a calcium chloride tube. The boat was weighed after the same lapse of time as in the experiments of Gomberg and van Stone.

The results we obtained do not completely correspond to the results described by Gomberg and van Stone. In our experiments too, the colored form of 3-methoxy-4-hydroxytriphenylmethyl lost weight much more rapidly than the colorless form; but, the lose in weight corresponding to that theoretically required for the removal of 1 mole of H_2O, 5.24%, was attained by us upon heating the colored form at 75° not for 2 hours 15 minutes, as in the experiments of Gomberg and van Stone, but for a much longer period – for 50 hours. Under these conditions, after the same period of time, the colorless 3-methoxy-4-hydroxytriphenylcarbinol showed a loss in weight that amounted in all to 0.6%.

However, our basic difference from Gomberg and van Stone lies elsewhere. According to Gomberg and his school, the loss in weight upon heating hydroxytriarylcarbinols must quantitatively characterize the degree of their conversion into the corresponding fuchsones; with a loss in weight corresponding to the theoretical amount, the carbinol taking part in the reaction is completely converted, according to Gomberg's opinion, into fuchsone. But it was precisely this assumption that Gomberg and van Stone failed to confirm – and this is the root of the error they made.

As we have already shown earlier [11], the thermal conversion of hydroxytriarylcarbinols into fuchsones does not take place quantitatively and is accompanied by destructive processes. We were once more able to satisfy ourselves of this by carrying out the experiments described above not in copper, as did Gomberg and van-Stone, but in glass apparatus. Because of this, we noted something that escaped the attention of the American investigators: at the cold, exit end of the tube in which the boat with the substances investigated was placed, we noticed a crystalline deposit of some yellow organic substance, which we could not, because of its small quantity, determine. But from this alone, it followed that the loss in weight of the heated carbinols was the result not only of their dehydration, but of some sort of destructive process; therefore, this loss of weight could not serve as a quantitative criterion of the dehydration of hydroxytriarylcarbinols.

In fact, upon further heating of the substance obtained from the colored 'desmotrope' of 3-methoxy-4-hydroxytriphenylcarbinol, beyond the point where loss in weight reached the theoretically calculated value, and the process of dehydration was seemingly complete, it continued to lose weight; after 100 hours, this loss in weight reached 8.4%, which was 1.6 times as high as the theoretically calculated 5.24%.

In order to confirm more fully the observations we had made, as described above, we decided to make a more thorough study of the product of reaction obtained from the colored 'desmotrope' at the moment when the loss in weight reached the theoretical value, and when, according to the views of Gomberg and van Stone, the contents of the boat must consist almost completely of 3-methoxyfuchsone; Gomberg and van Stone in their investigations also failed to do this – their other important omission.

Taking advantage of the properties of 3-methoxyfuchsone, which we have described [11], as being similar to those of the other fuchsones, to prepare a water-soluble colorless bisulfite derivative (the fuchsone thus differs from the corresponding hydroxytriarylcarbinol), we dissolved the material under investigation in alcohol, added to this solution a few milliliters of sodium bisulfite, and heated this mixture on the water bath at 50-60° for a few minutes. For purposes of comparison, we treated an equal weight of known 3-methoxyfuchsone under exactly the same conditions with the same amount of bisulfite. Still under identical conditions, we poured both solutions into water. From the known 3-methoxyfuchsone, we obtained a completely transparent colorless solution; from the substance under investigation we obtained an abundant precipitate, which showed that it was the original carbinol,

but colored slightly yellow.

Even with longer heating of the colored 'desmotrope' of 3-methoxy-4-hydroxyfuchsone, when its loss in weight was much greater than the theoretically calculated value, the residue in the boat even then did not completely form the bisulfite derivative of fuchsone; upon the treatment with bisulfite indicated above, this sample too gave a large quantity of the unchanged original carbinol in the precipitate.

Thus, all our experiments show that the loss in weight upon heating the hydroxytriarylcarbinols is not in the least a quantitative criterion for the degree of dehydration of these compounds; therefore the work of Gomberg and van Stone under consideration, contrary to the opinion of these authors, cannot serve as any sort of satisfactory argument either to defend the tautomerism of the hydroxyarylcarbinols, nor for the quinol formula of structure (V) for the colored 'desmotropes', as put forward by Gomberg.

Another argument advanced by Gomberg and his school in defense of the position cited was based on a comparison of the absorption curves for ultraviolet light of the colorless and colored 'desmotropes' of the hydroxytriarylcarbinols, and of the fuchsones which corresponded to them. These investigations, begun by Gomberg and Anderson in 1927 [9], were continued in 1929 by Anderson [10]. However, the conclusions from these investigations evoke considerable doubt.

In comparing the absorption curves of the colored 'desmotropes' and the corresponding fuchsones, Gomberg and Anderson noted that on the absorption curve of each of the colored 'desmotropes' under investigation there was a maximum at the same wave length where there was a maximum on the absorption curve of the corresponding fuchsone. In this Gomberg and Anderson saw a confirmation of the quinoid-like quinol structure of the colored desmotropes. But it is evident from these very experiments of Gomberg and Anderson that, on the one hand, the values of the maxima for the colored 'desmotropes' which are indicated above as being in agreement with regard to wave length are much smaller than for the corresponding fuchsones: and on the the other hand, the absorption curves of the colored 'desmotropes' have, in addition, other maxima as well, which correspond not to the respective fuchsones, but to the colorless hydroxytriarylcarbinols.

For purposes of illustration, we shall introduce a few data borrowed from the work of Anderson [10]. Table 1 gives a comparison of the wave lengths of the characteristic maxima of the absorption curves of both the 'desmotropes' and the fuchsones of corresponding structure for several compounds studied by Anderson.

TABLE 1

Substance		Wave lengths of maxima
4-hydroxy-triphenyl-carbinol	Colorless carbinol....	.....3500; 3582; 3701; 3754; 3802; 3850
	Colored 'desmotrope'..	2741; 3502; 3589; 3703; 3753; 3806; 3856.
	Fuchsone.....	2764.
3-methyl-4-hydroxytriphenyl-carbinol	Colorless carbinol....	..... 3493; 3577; 3692; 3748; 3849; 3946.
	Colored 'desmotrope'..	2743; 3496; 3583; 3700; 3751; 3854; 3950.
	Fuchsone.....	2740.
3-methoxy-4-hydroxytriphenyl-carbinol	Colorless carbinol....	..... 3483; 3548; 3708; 3747; 3858; 3951.
	Colored 'desmotrope'..	2648; 3479; 3548; 3702; 3751; 3848; 3941
	Fuchsone.....	2648

This table shows at a glance that the absorption curves of the colored desmotropes have maxima for wave lengths which correspond simultaneously to all the maxima both for the respective fuchsones and the respective colorless carbinols. Therefore, we cannot agree with the statements of Gomberg and Anderson that a comparison of the absorption curves in the ultraviolet satisfactorily confirms the existence of desmotropism in the hydroxytriarylcarbinol series, as well as the quinoid-like structure of the colored 'desmotropes'. From these very data of Gomberg and Anderson, we can with great probability draw the conclusion that the colored 'desmotropes' are mixtures of the corresponding colorless carbinols and fuchsones, and that the color of these 'desmotropes' is the result of the presence in them of an admixture of fuchsones. Ramar-Luka and Martynov, [12,13], who comparatively recently studied the absorption spectra in the ultraviolet of both modifications of 4-hydroxytriphenylcarbinol and of fuchsone, drew exactly this conclusion.

An important argument of Gomberg and his school in defense of the desmotropy of the hydroxytriarylcarbinols was that the colored forms or 'desmotropes', as these authors designated them, upon crystallization from aqueous acetic acid had a stable melting point and other properties, which did not change upon repeated crystallization from the same solvent. But, having advanced this argument, Gomberg was insufficiently critical both with regard to the various properties observed, and to the work of his predecessors.

Even in 1903, Auwers and Schroetter [2] noted that 4-hydroxytriphenylcarbinol obtained by crystallization from acetic acid in a colored form could be isolated, depending on the concentration of the acetic acid used for this purpose, in the form of crystals with a greater or lesser intensity of color, and with different melting points; in certain cases, the melting point equaled 138-139°, in others, 140°, and in a few they reached 143-144°. However, Auwers and Schroetter ascribed no significance to this observation; they saw the cause of these differences in melting point in the fact that 4-hydroxytriphenylcarbinol was converted into fuchsone by heating, and that therefore, the melting point of the substance could change slightly depending on the velocity of its determination, which was not always taken into account.

Gomberg and Anderson also had more than one opportunity of confirming the fact that the colored 'desmotropes' and other hydroxytriarylcarbinols, depending on the conditions of crystallization, differed in external characteristics. Thus, for example, they pointed out [9] that the 'quinoid tautomers' upon crystallization from 50, 60, and 70% acetic acid, or from 50 and 60% propionic acid, depending on the concentrations of these acids, were obtained with more or less intense color; the crystals obtained from the 70% acetic acid were much more yellow than the crystals from the 60%, and the latter more yellow than those from the 50% acid. The relation of colors of the crystals obtained from propionic acid at different concentrations was of the same kind. However, according to the claim of Gomberg and Anderson, the differences in the intensity of the color of the crystals could be explained by the character of the crystals alone, as solutions of all of them gave quantitatively identical absorption spectra. Therefore Gomberg and his school unconditionally accepted the supposed fact that the colored 'desmotropes' of hydroxytriarylcarbinol were completely individual substances with characteristic constants.

Our experiments have led us to completely different conclusions. We have crystallized 4-hydroxytriphenylcarbinol and 3-methoxy-4-hydroxytriphenylcarbinol from acetic acid of 40, 60, and 80% concentration. The crystals which separated out, after being dried to constant weight in a vacuum dessicator, showed different melting points when these were determined simultaneously in a single apparatus. The intensity of color of the crystals was also different. In order to make clear whether these differences actually depended only on the character of the crystals, and not on their containing different amounts of various colored substances, we dissolved

equal weights of the crystals obtained in benzene and made a colorimetric comparison of the intensity of color of the solutions. We shall give, for the sake of example, the data obtained for 3-methoxy-4-hydroxytriphenylcarbinol. Solutions obtained by dissolving 0.0005 mole of the substance in 10 ml of benzene differed noticeably in the intensity of their colors. To compare the solution of the product obtained by crystallization from 40% acetic acid and having m.p. 153-155°, we compared it colorimetrically with similar solutions of the substances obtained by crystallization from 60% and 80% acetic acid, and melting at 147-148° and 145-150°, respectively. The former of these had one half as intense a color as the substance from 40%, and the latter approximately one tenth. Having assumed that the intensity of the color both of the crystals and of the solutions made up from them depended on their content of 3-methoxyfuchsone, we dissolved 0.0005 mole of the latter in 10 ml of benzene, and took this solution as a standard (diluting it, for convenience in measurement, to 5 times its previous volume, and then making the proper correction in the colorimetric measurements) for additional colorimetric determinations. All the results obtained in this series of experiments are given in Table 2.

TABLE 2

No. of expt.	Yellow 4-hydroxy-3-methoxy-triphenylcarbinol, crystallized from acetic acid (%)	Melting point	Intensity of color of the benzene solution compared with	
			substance 1 (in %)	3-methoxyfuchsone (in %)
1	40	153-155°	100	1.1
2	60	147-148	50	0.55
3	80	145-150	9	0.1

We obtained similar results when we investigated the corresponding crystallized 4-hydroxytriphenylcarbinol.

It is clear from the data of Table 2 that contrary to the views of Auwers and Schroetter, on the one hand, and of Gomberg and his coworkers on the other, the colored 3-methoxy-4-hydroxytriphenylcarbinol obtained upon crystallization from acetic acid of different concentrations is not one and the same substance, but a mixture, differing both in melting point and in its content of the color-carrying substance; according to our suggestion, this is the related fuchsone. But the amount of the latter is very small; in this connection, it became clear to us why Gomberg and Anderson [10] found so low a maximum on the absorption curves of the colored 'desmotropes' of hydroxytriarylcarbinols at wave-lengths corresponding to the absorption maxima of the related fuchsones. On the other hand, with such small concentrations of fuchsone and such small maxima on the absorption curves, Gomberg and Anderson were unable, as we have shown above, to detect a quantitative difference in the intensity of the color of solutions by determining their absorption spectra, and this led to incorrect conclusions.

We found the first actual confirmation of our supposition, that the cause of the color of the colored forms of 3-methoxy-4-hydroxytriarylcarbinol is the 3-methoxyfuchsone contained in these forms in quantities that vary according to the concentration of the acetic acid from which the substance was crystallized, in the fact that substances completely similar to those described in Table 2 were obtained by us upon crystallization from acetic acid of the indicated concentrations not only of the colorless carbinol, but of the corresponding fuchsone. Upon crystallizing the latter from acetic acid of 40, 60, and 80% concentration in conditions corresponding to those for the crystallization of the carbinol, we obtained specimens of colored 3-methoxy-4-hydroxytriphenylcarbinol with the same properties as if the carbinol itself had been crystallized.

From this we may draw the probable conclusion that upon heating the acetic acid solutions of the hydroxytriarylcarbinols or their corresponding fuchsones, as well as mixtures of these substances, two processes may take place simultaneously – the hydration of the fuchsones, and the dehydration of the hydroxytriarylcarbinols. The mutual relations of these two opposing processes, which determine the conditions of equilibrium, and as a consequence, the content of fuchsone in the crystals that separate out, must depend on the concentration of acetic acid.

For experimental confirmation of this supposition, we carried out the following series of experiments. Using 0.001 mole each of fuchsone, 3-methoxyfuchsone, and the colorless hydroxytriarylcarbinols corresponding to both of these, that is, 4-hydroxytriphenylcarbinol and 3-methoxy-4-hydroxytriphenylcarbinol, we dissolved this amount in 100 ml of acetic acid of different concentrations, and boiled all the solutions obtained under identical conditions in small flasks fitted with reflux condensers for 30 minutes. After cooling, we determined, colorimetrically, the intensity of the color of each solution, taking the solution of the respective fuchsone in glacial acetic acid as a standard. The results are listed in Table 3.

TABLE 3

Concentration of acetic acid %	Intensity of color, starting with			
	Fuchsone (%)	4-hydroxytriphenylcarbinol (in %)	3-methoxy fuchsone (%)	3-methoxy-4-hydroxytriphenylcarbinol (%)
100	100	100	100	100
80	31	31	60	60
60	8.5	8	30	30
40	3	2.5	9 *	9 *

This series of experiments makes it very evident that upon heating with aqueous acetic acid, independent of whether the starting material is a given fuchsone or the corresponding colorless carbinol derivative, the identical mixture is formed in the solution, consisting of both these substances in quantities which depend on the concentration of acetic acid. It is thus completely indisputable that in acetic acid solutions both opposing processes actually take place – the hydration of the fuchsone, and the dehydration of the carbinol, leading to an equilibrium of the system, whose nature depends for each pair of substance on the concentration of the acid.

However, on comparing the data of Tables 2 and 3, we see that the content of fuchsone in acetic acid solution of a given concentration reached at the equilibrium condition is very much greater than the content of fuchsone in the solid substance that separates out from this solution during crystallization. Thus, for example, in the 40° acetic acid, the content of 3-methoxyfuchsone at equilibrium reaches 9%, but in the crystals that separate out from this solution it is only 1.1%. There is another striking example: in 80% acetic acid, the amount of 3-methoxyfuchsone at equilibrium is 60%, while in the crystals of 3-methoxy-4-hydroxytriphenylcarbinol obtained from this solution, it reaches only 0.1%. This is due to the different solubilities of the fuchsones and the hydroxytriarylcarbinols which correspond to them in organic solvents, among them acetic acid. As our investigations have shown, the fuchsones, as a rule, are much more soluble in organic solvents than are the hydroxytriarylcarbinols. In each individual case, the solubility relations of the given pair of these substances depend both on their structure and on the character of the solvent, and in the case of acetic acid, on its concentration.

* Upon further cooling in both cases there formed a precipitate of the colored carbinol, with m.p. 153-155°.

Therefore, the less soluble hidroxytriarylcarbinol separates out in the precipitate from acetic acid solution containing small, but variable amounts of fuchsone, amounts which depend on the concentration of the acetic acid. This gives the precipitated carbinol a color of different degrees of intensity.

It appeared that upon repeated crystallization from acetic acid of this already very pure carbinol we might expect its further purification. But this does not and cannot take place, as repeated heating with acetic acid, due to the opposing processes already mentioned, again forms an equilibrium system, from which there again precipitates a carbinol containing an admixture of fuchsone in the concentration customary for the given concentration of acid. Therefore, upon repeated crystallization of the hydroxytriarylcarbinols from acetic acid of a given concentration, there is obtained a mixture with a composition that is constant with regard to the corresponding carbinol and fuchsone, and a melting point constant for this composition; this has resulted in the assumption that these mixtures are chemical individuals, which were taken by Gomberg and his coworkers to be pure 'desmotropes'.

Of all the questions investigated by Gomberg and checked by us, there is one to which we cannot give a clear answer: why the pure colorless hydroxytriarylcarbinols are more stable to the action of heat in a jet of air than the colored carbinols containing an admixture of fuchsone. As we have already shown, the loss in weight during this action, which Gomberg accepted as a quantitative criterion characterizing the conversion of the carbinols into the corresponding fuchsones, cannot serve as such a criterion; it is related not so much to the dehydration of the hydroxytriarylcarbinols, apparently, as to their decomposition. But it has been known for a long time that the stability of a substance also depends on the degree of its purity; it is very probable that it is the admixture of adsorbed fuchsone, which, as a quinone derivative, may be the carrier of oxygen in oxidative destructive processes, and result in the loss of weight that Gomberg observed when the hydroxytriarylcarbinols were heated in a current of air.

On the basis of everything said above, we arrived at the conclusion that Gomberg's hypothesis of desmotropism of the hydroxytriarylcarbinols was completely unfounded, and that the colored modifications of the hydroxytriarylcarbinols, accepted by Gomberg as individual 'desmotropes', were in fact mixtures of the colorless hydroxytriarylcarbinols and the fuchsones corresponding to them, the fuchsones giving the mixtures their color, and resulting in a lowering of the melting point of the hydroxytriarylcarbinols.

In this connection, we faced the question: is it impossible to separate from such mixtures their component parts, or at least to isolate the colorless hydroxytriarylcarbinols from the fuchsones that accompany them? We found a partial answer to this question in the literature, among other places, in communications of Gomberg himself [4]. Back in 1913, when he was only beginning his investigations in the field of the triarylcarbinols, Gomberg noted that the colored 4-hydroxytriphenylcarbinol obtained by crystallization from aqueous acetic acid in the form of yellow crystals with m.p. 138-139°, and accepted by him as has already been indicated as an individual compound, upon further crystallization from alcohol grew gradually lighter, while the melting point of the substance rose. Thus, after two crystallizations of this substance, its m.p. reached 142-144°, and after a fourth crystallization, as high as 150°. But, being captive to the idea he had advanced, Gomberg could not correctly evaluate this observation, and decided that the lightening of the substance's color, as well as the rise in its melting point, was related to the slow isomerization of the colored 'desmotrope' to the colorless form upon heating in alcoholic solution.

But, having suggested this explanation, Gomberg was inconsistent, as both in the work cited and in further investigations he invariably suggested the idea

that upon heating it was precisely the colorless carbinol which isomerized to give the colored 'desmotrope'.

Our investigations have also confirmed the facts that upon heating the colorless hydroxytriarylcarbinols in organic solvents the solutions obtained gradually become yellow, and that the intensity of the color depends on the character of the solvent. But the cause of this is not the isomerization of the colorless carbinol into a colored 'desmotrope', but the partial thermal dehydration of the carbinol to produce the color of the fuchsone. Therefore, upon crystallization of the colored hydroxytriarylcarbinol from alcohol, or still better, from benzene, there takes place not the isomerization of the colorless carbinol into the colored 'desmotrope' as Gomberg supposed, but as is customary, purification during the crystallization of the substance, in this case. the hydroxytriarylcarbinol, from the accompanying impurities, in the case in question, from fuchsone. Gomberg might easily have confirmed this if he had paid attention to the fact that the solution which had been filtered from the precipitated lighter-colored crystals had an intense yellow color.

However, during the usual crystallization of hydroxytriarylcarbinols, even from neutral organic solvents, it is extremely difficult to obtain a completely colorless product. The cause of this lies in the fact that upon heating of the hydroxytriarylcarbinol solutions even in such solvents as absolute benzene, there still takes place, though slowly, the dehydration of the carbinol to give the fuchsone, and as a result, the coloring by the latter of the crystals which form. Consequently, in order to avoid this, it is necessary to carry out crystallization in the presence of agents which evoke the reverse process of hydration of the fuchsone, in particular in the presence of ammonia or pyridine, as Auwers and Schroetter [2], or Gomberg [4] recommend, or even to carry out the crystallization without accessory substances, but with the avoidance of heating.

Starting from these considerations, and wishing to purify 4-hydroxytriphenylcarbinol as much as possible from the fuchsone which colored it, we carried out the following seris of experiments. Using 0.0005 mole samples of the colored 4-hydroxytriphenylcarbinol obtained by crystallization from 20, 40, and 60% acetic acid, with melting points 129-132°, 139-140°, and 133-134° respectively, we digested them at room temperature, with periodic shaking, for a day, with 10 ml of absolute benzene. During this process, the solid substance, at first yellow, with a different intensity of color for each case of crystallization, was almost completely decolorized; the benzene filtrates, however, were colored, the intensity of color being compared colorimetrically with the standard solution obtained with pure fuchsone. The results thus obtained are listed in Table 4.

This series of experiments showed that simple treatment with benzene could to a considerable extent wash out of the colored 4-hydroxytriphenylcarbinol the fuchsone impurity which caused its color. On the other hand, the data of Table 4 show once more (cf. Table 2) that the content of fuchsone in the carbinol crystals obtained by crystallization from acetic acid depends on the concentration of the latter.

TABLE 4

Concentration of acetic acid used for crystallization, %	Melting point of the crystals	Content of fuchsone in benzene extract (in %)
20	129-132°	2.1
40	139-140	0.5
60	133-134	0.3

The 4-hydroxytriphenylcarbinol could be obtained almost completely colorless, starting with the colored product, if a small quantity of the latter was dissolved without heating in a large amount of benzene, and the solution obtained was concentrated in vacuum without heating. The carbinol precipitates almost without color, as it is very slightly soluble in cold benzene, but the mother liquour remains colored yellow.

The 4-hydroxy-3-methoxytriphenylcarbinol is even easier to purify by crystallization from benzene.

Finally, we decided to separate the hydroxytriarylcarbinols from the fuchsones which accompanied them in the colored products by utilizing, not the different solubilities of these substances in organic compounds, but their different chemical properties, in particular, their behavior with bisulfite.

As we have already indicated [1], fuchsones react with bisulfite to give the bisulfite derivatives, which are completely soluble in water. The hydroxytriarylcarbinols do not react with bisulfite provided the conditions of the reaction do not result in their preliminary dehydration to fuchsones; therefore, on the basis of the experiments described above, the use of acetic acid as solvent was completely excluded from the reaction of hydroxytriarylcarbinols with bisulfite. We carried out our experiments in the following manner: 0.5 g of the colored hydroxytriarylcarbinol which had been crystallized from acetic acid (4-hydroxytriphenylcarbinol or 3-methoxy-4-hydroxytriphenylcarbinol) was dissolved in 10 ml of alcohol. For purposes of control, we at the same time dissolved in the same quantities of alcohol 0.5 g portions of the corresponding colorless hydroxytriarylcarbinols and fuchsones. To each of these solutions we added an equal volume of 10% bisulfite solution which had been preheated to 80°. The mixtures obtained were set aside for a short time, until they were completely decolorized, in warm water; then each was poured into 100 ml of water. With the fuchsone, we obtained completely transparent and colorless solutions (bisulfite derivatives); with the colorless hydroxytriarylcarbinols we obtained on the other hand a copious white residue of the same substance. Under the same conditions, with the colored carbinols under investigation, we also obtained a colorless carbinol residue; obviously, the fuchsone which accompanied the latter in the original product was converted into the bisulfite derivative, which went into solution.

These experiments give one more, and as it seems to us, the most incontrovertible demonstration of the fact that the colored hydroxytriarylcarbinols are not individual compounds, but mixtures of the colorless true triarylcarbinols with small quantities of the fuchsones structurally related to them. The hypothesis advanced by Bistrzhitsky and supported and developed with especial persistency by Gomberg, that hydroxytriarylcarbinols exist in two individually separable desmotropic forms, the colorless and the colored, is incorrect.

SUMMARY

Upon critical consideration and experimental testing of the arguments advanced by Gomberg and his school in defense of the desmotropism of 4-hydroxytriphenylcarbinol and its derivatives, we have found the following.

1. The loss in weight of the hydroxytriarylcarbinols upon heating cannot be a quantitative criterion determining the degree of transformation of these substances into the corresponding fuchsones, despite Gomberg's acceptance of it; under the conditions of experiment, not only does dehydration of the hydroxytriarylcarbinol take place, but destructive process as well. Therefore, a comparison of the loss in weight of the colorless and the colored modifications of hydroxytriarylcarbinols cannot be utilized as an incontrovertible method for the determination of their structures.

2. A comparison of the absorption curves of the colorless and the colored forms of the hydroxytriarylcarbinols and the fuchsones corresponding to them gives no satisfactory basis for accepting the colored modifications as individual substances or 'desmotropes', as Gomberg suggests.

3. During the crystallization of the hydroxytriarylcarbinols from aqueous

acetic acid, two mutually opposed processes take place — the dehydration of the hydroxytriarylcarbinols and the hydration of the fuchsones; at equilibrium, a mixture of these substances is obtained in proportions that depend on the concentration of acetic acid; the colored hydroxytriarylcarbinols that precipitate from these solutions are distinguished by their melting points and the intensity of their color, and contain quantities of adsorbed fuchsone that vary in dependence upon the concentration of acid, and determine the color.

4. As a result of the opposing processes, repeated crystallization from acetic acid of definite concentration leads to the isolation of colored hydroxytriarylcarbinols with constant melting point and intensity of color; this gives no ground, however, for accepting these products as individual substances.

5. Starting with the colored hydroxytriarylcarbinols, we can almost completely wash out the fuchsone impurities that cause the color, utilizing the better solubility of the fuchsones in such organic solvents as alcohol and benzene.

6. From the colored hydroxytriarylcarbinols we can obtain colorless, pure compounds by removing the fuchsone impurities in the form of their bisulfite derivatives.

On the basis of what has been said above, we can draw the conclusion that the theory of the desmotropism of the hydroxytriarylcarbinols, proposed by Bistrzhitsky and consistently supported and developed by Gomberg and his school, is incorrect; the colored modifications of the hydroxytriarylcarbinols accepted by Gomberg as individual substances, as 'desmotropes' of the hydroxytriarylcarbinols, are actually mixtures of the colorless hydroxytriarylcarbinols and the corresponding fuchsones.

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THE TRANSFORMATION OF α- AND β-ALKYLFURANIDINES INTO THE CORRESPONDING α- AND β-ALKYLPYRROLIDINES. XXVI

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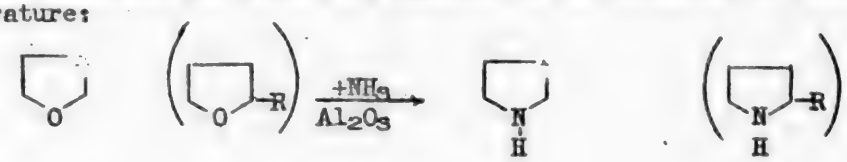
In the present paper, we have considered the transformation of α- and β-alkylfuranidines (tetrahydrofurans) into the corresponding α- and β-alkylpyrrolidines by the action on the former of ammonia in the presence of aluminum oxide at high temperature:



R = $-CH_3$, $-C_2H_5$, $-C_3H_7$, $-C_4H_9$

The purpose of the work was not only to obtain previously undescribed α- and β-alkyl homologs of pyrrolidine, but also to compare the behavior of α-alkyl- and β-alkylfuranidines in this reaction, as well as to clear up the question of the influence of the size of the alkyl radical of the side chain in the original furanidines on the yield of final products of the reaction.

The experimental data obtained in the present work are given in the table.

Comparative data on the transformation of alkyl homologs of furanidine (α- and β- series) to the corresponding alkyl homologs of pyrrolidine.

Expt. No.	Starting Material	Amount g	t° of reaction	Reaction products	Yield g	Yield, % of theory
1	Furanidine [1].....	10	400°	Pyrrolidine.....	4.6	46.5
2	α-Methylfuranidine [2]	6	400	α-Methylpyrrolidine	1.6	27
3	α,α'-Dimethylfuranidine [3].....	11	400	α-α'-Dimethylpyrrolidine.....	1.9	17.5
4	α-Ethylfuranidine [4]..	10.2	400	α-Ethylpyrrolidine.	0.9	9.0
5	α-Propylfuranidine.....	8.3	350	α-Propylpyrrolidine	0.8	10.0
6	α-Butylfuranidine.....	15.8	350	α-Butylpyrrolidine.	1.6	10.0
7	β-Methylfuranidine.....	3.0	350	β-Methylpyrrolidine	0.9	30.0
8	β-Ethylfuranidine.....	9.4	350	β-Ethylpyrrolidine	1.8	19.0
9	β-Propylfuranidine.....	9.6	350	β-Propylpyrrolidine	1.5	15.0
10	β-Butylfuranidine.....	8.6	350	β-Butylpyrrolidine	1.0	12.0

From the data of the table it is clear that the yields of both the α-alkyl and the β-alkylpyrrolidines decreased with an increase in the number of carbon atoms in the side chain of the original alkylfuranidines.

With regard to the dependence of the yields of the alkylpyrrolidines upon the

position of the side chain in the ring, we must observe that in the cases here studied, as well as in those previously described, of the production of α-alkyl- and β-alkyl thiophanes [5], the compounds of the β-series are obtained in slightly better yields than the compounds of the α-series.

EXPERIMENTAL

The transformation of alkylfuranidines into the corresponding alkylpyrrolidines took place under the following conditions: the alkylfuranidines were conducted with a velocity of 6 to 7 drops per minute in a strong stream of ammonia through a tube filled with aluminum oxide and heated to 350°; fresh catalyst was required for each experiment. The catalyst was saturated with solid potassium hydroxide and extracted with ether. After the ether extract had been dried over molten caustic potash, the ether was driven off (with a dephlegmator) and the residue fractionated.

1) β-Methylpyrrolidine. For the reaction with ammonia, 3 g of β-methylfuranidine was used (b.p. 86-86.5° at 750 mm; d_4^{20} 0.8659; n_D^{20} 1.4111 [8]). Upon distillation of the reaction product, the temperature quickly rose to 102°, and in the interval from 102-112° 1 g of crude β-methylpyrrolidine was collected; an insignificant residue remained in the distilling flask. Upon repeated distillation above metallic sodium, pure β-methylpyrrolidine was obtained (yield 0.9 g, 30% of the theoretical). This had the following constants:

B.p. 102-103° (727 mm); d_4^{20} 0.8569; n_D^{20} 1.4480; MR_D 26.61.
$C_5H_{11}N$. Calculated MR_D: 26.69.
Melting point of the picrate (after recrystallization from alcohol) 106.5-107.5°.

3.942 mg substance: 0.564 ml N_2 (19°, 755 mm).
4.630 mg substance: 0.660 ml N_2 (20°, 755 mm).
Found %: N 16.61, 16.50.
$C_5H_{11}N$. Calculated %: N 16.45.

The literature gives for β-methylpyrrolidine: Oldach [7]: b.p. 103-105°; d_4^{20} 0.8654; Melting point of the picrate (from water) 105°; Spath and Breusch [8]: melting point of the picrate (from alcohol) 106°.

2) β-Ethylpyrrolidine. For the reaction with ammonia 9.4 g of β-ethylfuranidine was taken (b.p. 115.5-116.5° at 748 mm; d_4^{20} 0.8601 [8]; n_D^{20} 1.4204). Upon distillation of the product of reaction, the temperature quickly rose to 127°; in the interval from 127 to 137°, 3.5 g of the crude β-ethylpyrrolidine came over. Upon repeated distillation, β-ethylpyrrolidine came over at 131° (747 mm). Yield 1.8 g, 19% of the theoretical.

B.p. 131° (747 mm); d_4^{20} 0.8579; n_D^{20} 1 4501; MR_D 31.27
$C_6H_{13}N$. Calculated MR_D 31.31.
Melting point of the picrate (after recrystallization from alcohol) 101-101.5°.

4.150 mg substance: 0.501 ml N_2 (18°, 755 mm).
5.341 mg substance: 0.648 ml N_2 (18° 755 mm).
Found %: N 14.08, 14.08.
$C_6H_{13}N$. Calculated %: N 14.13.

β-Ethylpyrrolidine is not described in the literature.

3) β-Propylpyrrolidine. For the reaction with ammonia 9.6 g of β-propylfuranidine was taken (b.p. 141.1-141.8 at 748 mm; d_4^{20} 0.8555· n_D^{20} 1.4222 [8]). Upon distillation of the product of reaction, a fraction was selected with b.p. 155-170°, and after repeated fractionation, β-propylpyrrolidine was isolated from it. Yield 1.5 g (15% of the theoretical):

B.p. 158° (754 mm); d_4^{20} 0.8535; n_D^{20} 1.4521; MR_D 35.77.
$C_7H_{15}N$. Calculated MR_D 35.92.
Melting point of the picrate (after recrystallization from alcohol) 100.5-101°.

4.378 mg substance: 0.467 ml N_2 (20°, 754 mm).
5.624 mg substance: 0.597 ml N_2 (19°, 753 mm).
Found %: N 12.33, 12.30.
$C_7H_{15}N$. Calculated %: N 12.38.

The literature gives for β-propylpyrrolidine; V.V.Longinov [8]: b.p. 158-160° (746 mm); d_4^{20} 0.8450; n_D^{20} 1.4469.

4. β-Butylpyrrolidine. For the reaction with ammonia, 8.6 g of β-butylfuranidine was taken (b.p. 167.1-167.8° at 757 mm; d_4^{20} 0.8612; n_D^{20} 1.4323 [8]). Upon distillation of the product of reaction, a fraction was collected which distilled over at from 160 to 185°. We did not succeed in isolating β-butylpyrrolidine in pure form by repeated distillation of this fraction because of contamination with a small quantity of β-butylfuranidine which had not reacted. Therefore, the pure base was isolated in the following manner: the fraction with a wide boiling range was treated with an excess of hydrochloric acid (1:2). The solution of hydrochloride of the base that was obtained (after extraction of impurities with ether) was evaporated to dryness. The action of a concentrated solution of caustic potash on the dry hydrochloride released the β-butylpyrrolidine, and this was extracted with ether. After the ether extract had been dried and the ether driven off, the β-butylpyrrolidine was distilled. It came over at 179-179.2° (729 mm). Yield 1 g, or 12% of the theoretical.

d_4^{20} 0.8463; n_D^{20} 1.4531; MR_D 40.62.
$C_8H_{17}N$. Calculated MR_D: 40.54.
Melting point of the picrate (after recrystallization from benzene): 76-76.5°.

3.776 mg substance: 0.357 ml N_2 (18°, 758 mm).
4.893 mg substance: 0.463 ml N_2 (19°, 755 mm).
Found %: N 11.06, 11.01.
$C_8H_{17}N$. Calculated %: N 11.01.

β-Butylpyrrolidine is not described in the literature.

5. α-Propylpyrrolidine. For the reaction with ammonia, 8.3 g of α-propylfuranidine was taken (b.p. 132-133° at 738 mm; d_4^{20} 0.8547; n_D^{20} 1.4237 [5]). Upon distillation of the product of reaction, the temperature quickly rose to 130°, and a fraction was collected in the range from 130-170°. This fraction was treated in the same manner as the fraction in the preceding experiment to give α-propylpyrrolidine. Yield 0.8 g, 10% of the theoretical.

B.p. 149-151° (731 mm); d_4^{20} 0.8259; n_D^{20} 1.4489; MR_D 36.72.
$C_7H_{15}N$. Calculated MR_D: 35.92.

5.660 mg substance: 0.598 ml N_2 (16°, 754 mm).
3.115 mg substance: 0.330 ml N_2 (17°, 754 mm).
Found %: N 12.37, 12.45.
$C_7H_{15}N$. Calculated %: N 12.38.

The literature gives for α-propylpyrrolidine: Hess [10]: b.p. 145-150° (765 mm); Gabriel [11]: m.p. of the picrate 104-104.5°.

6. α-Butylpyrrolidine. For the reaction with ammonia, 15.8 g of α-butylfuranidine was taken (b.p. 158-159° at 750 mm; d_4^{20} 0.8554; n_D^{20} 1.4287 [5]). Upon distillation of the product of reaction, a fraction was collected which came over from 150 to 180°. As a result of the treatment of this fraction in the same way as in the two preceding experiments, α-butylpyrrolidine was obtained. Yield 1.6 g, or 10% of the theoretical.

B.p. 173.5-174.5° at 741 mm; d_4^{20} 0.8277; n_D^{20} 1.4490; MR_D 41.22.
$C_8H_{17}N$. Calculated MR_D: 40.54.

3.615 mg substance: 0.340 ml N_2 (18°, 754 mm).
3.600 mg substance: 0.340 ml N_2 (18°, 755 mm).
Found %: N 10.95, 11.01.
$C_8H_{17}N$. Calculated %: N 11.01.

The literature gives for α-butylpyrrolidine: Blaise and Cornillot [12]: b.p. 67° (18 mm); m.p. of chloraurate 91°; of chloroplatinate, 123°; Hess [13]: b.p. 154-156° (753 mm); m.p. of chloraurate 145°; of chloroplatinate, 178° (with decomp.); G.P.Menshikov and E.S.Zhdanovich [14]; b.p. 171-172°.

SUMMARY

1. In the present paper, we have described the preparation of a series of β- and α-alkylpyrrolidines by the reaction of the corresponding alkylfuranidines (tetrahydrofurans) with ammonia in the presence of aluminum oxide at 350°. In this manner we have synthesized: β-methyl-, β-ethyl-, β-propyl-, and β-butylpyrrolidines, as well as the α-propyl- and a-butylpyrrolidines.

2. β-Alkylpyrrolidines have higher boiling points, specific gravities, and indexes of light refraction that their isomeric α-alkylpyrrolidines.

3. The yields of both α- and β-alkylpyrrolidines decreased with an increase in the number of carbon atoms in the side chain of the original oxygen-containing heterocycles.

4. β-Alkylpyrrolidines were obtained in somewhat better yields than the α-alkylpyrrolidines.

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*See Cb translation p. a167 ff.
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PHOTOREACTIONS OF IODOORGANIC COMPOUNDS

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There are indications in the literature [1] of the formation of radicals by the removal of halogens from aryl halides by means of metals. As a result of the action of sodium or copper in ether upon the halides, the formation of a small quantity of aromatic hydrocarbons takes place due to the acquisition by the radicals of hydrogen from the solvent. Upon heating iodobenzene in a sealed tube with ethyl benzoate, there takes place a reaction of amphoteric substitution which is characteristic for the radicals, with the formation of the 2- and 4-phenylbenzoates. On the other hand, radicals are formed during the photolysis of mercuro-organic compounds [2]. It appeared of interest to investigate the reaction of mercuro-organic compounds with iodobenzene or other iodo-organic derivatives; the formation of two radicals was to be expected. Thus, in benzene solution, diphenylmercury and iodobenzene react according to the equation:

$$(C_6H_5)_2Hg + C_6H_5I \longrightarrow C_6H_5HgI + C_6H_5{-}C_6H_5.$$

Actually, the reaction takes place in a more complicated manner than the above overall equation indicates. If instead of diphenylmercury we take ditolylmercury, we may expect the formation of methyldiphenyl; however, at the end of the reaction we find diphenyl and ditolyl. The reaction, apparently, takes place in the following manner: at first the formation of two radicals takes place:

$$Ar_2Hg + C_6H_5I \longrightarrow ArHgI + Ar + C_6H_5;$$

these do not react with the benzene solvent, and dimerize to give Ar—Ar and diphenyl.

The photoreaction in solutions of alcohols (methyl, ethyl, and isopropyl) takes place in a completely different manner. Here there is also a primary process of formation of radicals, which then react with the alcohols, removing hydrogen to form benzene or toluene from diphenyl- or ditolylmercury and benzene or iodobenzene. Consequently, in this case too the radicals react entirely as in other photoreactions of diphenyl- and ditolylmercury, and as they react during the heating of their alcoholic solutions at high temperature [3].

In general, the reaction takes place according to the mechanism:

$$Ar_2Hg + C_6H_5I \longrightarrow ArHgI + Ar- + C_6H_5-;$$
$$C_6H_5- + Ar- + CH_3OH \longrightarrow C_6H_6 + ArH + CH_2O,$$

where

$$Ar = C_6H_5- \text{ or } CH_3C_6H_4-.$$

The benzyl radical behaves differently. In the reactions of dibenzylmercury, it always dimerizes to give dibenzyl, regardless of the solvent [4]. It appeared of interest to elucidate the behavior of the benzyl radical, which must appear when iodobenzene is replaced by benzyl iodide or benzyl chloride in the reactions listed above.

Actually, in this case too the benzyl radical dimerizes to give dibenzyl. The

reaction in alcoholic solution takes place in a manner similar to that indicated above.

In benzene solution, diphenylmercury and benzyl iodide form phenylmercuric iodide, diphenyl, and dibenzyl.

Thus, in all the reactions, the radicals obtained from iodo-organic compounds give results completely analogous to those previously obtained.

EXPERIMENTAL

The Photoreaction of Diphenylmercury and Iodobenzene in Benzene

There were used in the reaction: 2.0 g of diphenylmercury, 1.1 g of iodobenzene, and 20 ml of benzene. Illumination was continued for 60 hours. The reaction was carried out in a quartz test tube. The white precipitate formed was filtered off and recrystallized from dichloroethane. There was obtained 1.5 g of phenylmercuric iodide with m.p. 276°, without depression when mixed with the pure substance (70% of theory). The benzene was distilled away from the filtrate, and the residue distilled with steam to give 0.65 g of diphenyl with m.p. 70°; a mixed test gave no depression. After the steam distillation there remained 0.4 g (20%) of diphenylmercury with m.p. 123°, without depression when mixed with the pure compound. Therefore, the products of reaction were phenylmercuric iodide and diphenyl.

The Photoreaction of p-Ditolylmercury and Iodobenzene in Benzene

A solution of 1.75 g of p-ditolylmercury, 0.9 g of iodobenzene, and 20 ml of benzene was illuminated for about 60 hours. The precipitate of p-tolylmercuric iodide obtained was filtered off and weighed. The weight was 1.5 g.

To remove unchanged p-ditolylmercury, the precipitate was washed with hot xylene; pure p-ditolylmercury then remained, in an amount equal to 1.4 g (74%). After recrystallization from dichloroethane, the m.p. was 218-219°. The benzene was driven off from the filtrate; there remained a mixture of crystals of diphenyl and ditolyl. This mixture was oxidized with an alkaline solution of permanganate and the diphenyl was distilled directly from the same flask with steam to the amount of 0.2 g. M.p. 70°, without depression when mixed with the pure product. The oxidized solution was filtered and concentrated. Hydrochloric acid was added, and a precipitate of 0.1 g of diphenyldicarboxylic acid was formed. This decomposed at high temperature, and gave diphenyl upon calcining with CaO. The diphenyl which had distilled off was recrystallized; the m.p. was 70°, and there was no depression upon mixing with the pure compound.

Therefore, the reaction gave: p-tolylmercuric iodide, diphenyl, and ditolyl.

The Photoreaction of Diphenylmercury and Iodobenzene in Methyl Alcohol

A solution of 2.0 g of diphenylmercury, 1.2 g of iodobenzene, and 20 ml of methyl alcohol was illuminated for 24 hours.

There was obtained 1.9 g of phenylmercuric iodide, which after recrystallization from tetrachloroethane gave m.p. 273°, with no depression upon mixing with the pure substance. The alcoholic solution was distilled, and the first portion diluted with water. From it there was obtained 0.4 ml of benzene, which gave m-dinitrobenzene upon nitration, m.p. 91-92°.

In another portion formaldehyde was found (qualitative reaction with fuchsine-sulfurous acid). The residue was distilled with steam; after the distillation, there remained 0.2 g of phenylmercuric iodide. There was obtained a total of 2.1 g (92.5% of theory) of phenylmercuric iodide. Consequently, the products of reaction were phenylmercuric iodide, benzene, and formaldehyde.

The Photoreaction of Diphenylmercury and Iodobenzene in Ethyl Alcohol*

A solution of 2.0 g of diphenylmercury, 1.6 g of iodobenzene, and 30 ml of ethyl alcohol was illuminated about 24 hours. There was obtained 1.6 g (73% of theory) of phenylmercuric iodide with m.p. 272° after recrystallization from tetrachloroethane. The alcoholic solution was distilled, and from the first portion, after dilution with water, benzene was isolated. This was nitrated to give 0.25 g of m-dinitrobenzene with m.p. 89°, and no depression of the m.p. upon mixing with the pure product.

Acetaldehyde was determined in a second portion of the aqueous-alcoholic solution (qualitative reaction to give silver mirror, and reaction with fuchsine-sulfurous acid).

Therefore, the products of the reaction were: phenylmercuric iodide, benzene, and acetaldehyde.

The Photoreaction of Diphenylmercury and Iodobenzene in Isopropyl Alcohol

A solution of 1.0 g of diphenylmercury, 2.7 g of iodobenzene, and 10 ml of isopropylalcohol was illuminated for about 24 hours.

There was obtained from the reaction 1.1 g of phenylmercuric iodide (100% of theory), giving m.p. 272° after recrystallization from tetrachloroethane. The alcoholic solution was distilled, and the first portion, after dilution with water, gave 0.5 ml of benzene, which was nitrated to give m-dinitrobenzene with m.p. 89°, and no depression upon mixing with the pure compound.

Acetone was determined in the second portion of the alcoholic solution (qualitative reaction with nitroprusside). The products of reaction were: phenylmercuric iodide, benzene, and acetone.

The Photoreaction of o-Ditolylmercury and Iodobenzene in Methyl Alcohol

A solution of 2 g of o-ditolylmercury, 1.2 g of iodobenzene, and 20 ml of methyl alcohol was illuminated about 60 hours. The precipitate was filtered off. The filtrate was distilled on the water bath, and benzene and toluene extracted from the distillate with ether.

Formaldehyde was found in the aqueous-alcoholic solution (qualitative reaction to give silver mirror, and reaction with resorcinol)[5]. After removal of the ether, the residue was oxidized with an alkaline solution of permanganate, and then acidified and steam distilled. Benzene distilled over with the first portion of water; it was extracted with carbon tetrachloride and nitrated. There was thus obtained 0.2 g of m-dinitrobenzene with m.p. 89°, with no depression of the m.p. when mixed with the pure product. The oxidized solution was filtered and hydrochloric acid added to the filtrate; benzoic acid precipitated, with m.p. 121-122°, and no depression of the m.p. in a mixed test.

After the steam distillation, there remained in the condenser and in the flask a residue which was extracted with hot acetone to give 0.25 g (15%) of o-ditolylmercury with m.p. 105°, with no depression on mixing with the pure compound. In the same residue, a small amount of mercuric iodide was observed.

The weight of the o-tolylmercuric iodide precipitate obtained upon filtration was 1.55 g (73% of theory); as this compound has not been described in the literature, it was analyzed for its mercury content.

Analysis for mercury: 0.493 g substance: 0.261 g HgS.
Found %: Hg 45.6
C_7H_7HgI. Calculated %: Hg 47.8.

* Student Z. Marchinova shared this part of the work.

After recrystallization from dichloroethane the melting point was found to be 257°. Therefore, the products of the reaction were: o-tolylmercuric iodide, benzene, toluene, and formaldehyde.

The Photoreaction of Diphenylmercury and Benzyl Iodide in Methyl Alcohol

There were taken for the reaction: 2 g of diphenylmercury, 1.2 g of benzyl iodide, and 25 ml of methyl alcohol. The illumination was continued for about 80 hours.

The products of reaction included a precipitate of phenylmercuric iodide, which was filtered off and weighed; the weight of the precipitate was 2.1 g. To remove the unreacted diphenylmercury, the precipitate was washed with acetone. The weight of pure phenylmercuric iodide was 1.9 g (86% of theory). After recrystallization from dichloroethane, the m.p. was 276°. A mixed test showed no lowering of the m.p. After removal of the acetone, 0.17 g of unreacted diphenylmercury with m.p. 124° was obtained.

The methyl alcohol was distilled off from the filtrate, diluted with water, and treated with carbon tetrachloride. The benzene extracted was nitrated. Nitration gave 0.36 g of m-dinitrobenzene (45% of theory) with m.p. 87-88°. A mixed test with the pure product gave no lowering.

The aqueous-alcoholic solution was investigated for the presence of formaldehyde, which was observed by the qualitative reactions of silver mirror formation, and behavior with resorcinol, and was determined quantitatively by the polarographic method.

The polarographic determination of formaldehyde was carried out with 0.1 N NaOH; it had a reducing action with half-wave potential $\pi^{1}/_{2}$ = 1.1 volt with respect to the saturated calomel electrode. The formaldehyde content of the products of decomposition appeared equal to 0.05 g. The precipitate obtained after driving off the methyl alcohol was distilled with steam; it gave 0.38 g (95% of theory) of dibenzyl, with m.p. 52°, and no lowering of the m.p. upon mixing with the pure substance, and 0.05 g of diphenylmercury. A total of 0.22 g of diphenylmercury, or 11%, did not enter into reaction. Therefore, the products of photolysis were: phenylmercuric iodide, benzene, dibenzyl, and formaldehyde.

The Photoreaction of Diphenylmercury and Benzyl Chloride in Methyl Alcohol

A solution of 2 g of diphenylmercury, 0.7 g of benzylchloride, and 25 ml of methyl alcohol was illuminated for about 80 hours.

The reaction gave a precipitate of crude phenylmercuric chloride, whose weight was 1.7 g. After removal of the unreacted diphenylmercury with acetone, 1.4 g (84%) of phenylmercuric chloride was obtained; after recrystallization from dichloroethane this had m.p. 257°, with no lowering of the m.p. upon mixing with the pure compound. After removal of the acetone by distillation, 0.25 g of diphenylmercury was obtained with m.p. 123-124°. The methyl alcohol was driven off from the filtrate, diluted with water, and benzene extracted from it with carbon tetrachloride; the benzene was nitrated to give 0.25 g (31% of theory) of m-dinitrobenzene with m.p. 88°, and no lowering of the m.p. in a mixed test.

The aqueous-alcoholic solution was investigated for formaldehyde, which was detected by silver mirror formation, and determined quantitatively by the polarographic method. The polarographic determination of formaldehyde was made with 0.1 N NaOH, where it had a reducing action with half-wave potential $\pi^{1}/_{2}$ = 1.1 volt with respect to a saturated calomel electrode. The formaldehyde content in the products of reaction appeared equal to 0.045 g. From the precipitate obtained after removal of the methyl alcohol and distillation with steam, 0.2 g (50% of theory) of dibenzyl was

obtained,, with m.p. 52°, and no lowering upon mixing with the pure product. In the residue there was found 0.07 g of diphenylmercury. A total of 0.32 g (16%) of diphenylmercury was recovered after the experiment. Therefore, the products of this photoreaction were: phenylmercuric chloride, benzene, dibenzyl, and formaldehyde.

The Photoreaction of o-Ditolylmercury and Benzyl Iodide in Methyl Alcohol

A solution of 2 g of o-ditolylmercury, 1.1 g of benzyl iodide, and 20 ml of methyl alcohol was illuminated about 60 hours. The precipitate of crude o-tolylmercuric iodide obtained (1.9 g) was washed with hot acetone to remove the unreacted o-ditolylmercury. The quantity of the latter was 0.15 g (7%), and in the residue, 1.75 g (83% of theory) of pure-o-tolylmercuric iodide was obtained, with m.p. 257°.

The methyl alcohol was carefully distilled from the filtrate; 0.3 g of toluene came over with it, and was further oxidized to benzoic acid.

From the residue, steam distillation gave 0.21 g of dibenzyl with m.p. 52°, and no m.p. depression upon mixing with the pure compound. Therefore, the products of the reaction were: o-tolylmercuric iodide, toluene, and dibenzyl.

The Photoreaction of Diphenyl and Benzyl Iodide in Benzene

A solution of 2 g of diphenylmercury, 1.2 g of benzyl iodide, and 20 ml of benzene was illuminated for about 80 hours.

The precipitate of phenylmercuric iodide obtained was filtered off and washed with acetone until it was free of unreacted diphenylmercury. The weight of the phenylmercuric iodide equaled 1.64 g (70% of theory), after recrystallization from dichloroethane. The m.p. was 274°, with no depression upon mixing with the pure compound. From the acetone solution, 0.16 g of diphenylmercury crystallized out, with m.p. 123°.

The benzene was driven off from the filtrate, and the residue steam-distilled. After the steam-distillation, there remained 0.3 g of diphenylmercury. A total of 0.46 g (23%) of diphenylmercury was recovered after the experiment. Distillation gave crystals with m.p. 44°, which represented a mixture of diphenyl and dibenzyl. These crystals were oxidized with an alkaline solution of permanganate. The reaction mixture was steam distilled to separate the diphenyl; the amount was 0.2 g, the m.p. 70°, with no depression upon mixing with the pure compound. After distillation of the diphenyl, the oxidized solution was filtered and concentrated; hydrochloric acid precipitated from it benzoic acid with m.p. 121-122°.

Therefore, the reaction products were: phenylmercuric iodide, diphenyl, and dibenzyl.

SUMMARY

1. Diphenylmercury and iodobenzene in benzene solution, upon illumination with ultraviolet light, react to give phenylmercuric iodide and diphenyl. The same substances in alcoholic solutions give phenylmercuric iodide, benzene, and the dehydrogenation product of the alcohol — aldehyde or ketone.

2. The photoreaction of ditolylmercury and iodobenzene in benzene solution gives tolylmercuric iodide, diphenyl, and ditolyl. In methyl alcohol solution, the same substances give tolylmercuric iodide, benzene, toluene, and formaldehyde.

3. Diphenylmercury and benzyl iodide in benzene also give phenylmercuric chloride, dibenzyl, and diphenyl.

4. In methyl alcohol, diphenylmercury and benzyl chloride or iodide give the phenylmercuric halide, dibenzyl, benzene, and formaldehyde.

5. A mechanism for the photoreaction of diarylmercury and iodine derivatives has been proposed.

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*See CB translation p. 711 ff.

THE PHOTOREACTIONS OF METALLO-ORGANIC COMPOUNDS OF MERCURY IN SOLUTION

IV. THE PHOTOREACTIONS OF o-DITOLYLMERCURY

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In previous communications [1], we have investigated the photoreactions of diphenyl- and dibenzylmercury in various organic solvents. In the present work, we have made a study of the photoreaction of o-ditolylmercury in methanol, the monomethyl ether of ethylene glycol, ethyl formate, 1,2-dichloroethane, chloroform, and carbon tetrachloride.

As a rule, the photoreactions of o-ditolylmercury are concluded more rapidly than those of diphenylmercury. The photoreaction of o-ditolylmercury in methyl alcohol takes place quantitatively with the formation of toluene, mercury, and formaldehyde, according to the equation:

$$(CH_3C_6H_4)_2Hg + CH_3OH \xrightarrow{h\nu} 2C_6H_5CH_3 + Hg + CH_2O.$$

In monoethyl ether of ethylene glycol and in ethyl formate, the photoreaction also proceeds very smoothly, with the formation of toluene, mercury, and aldehyde. For example, for the nomoethyl ether of ethylene glycol, we may write the reaction in this way:

$$HOCH_2CH_2OC_2H_5 + (CH_3C_6H_4)_2Hg \xrightarrow{h\nu}$$

$$2CH_3C_6H_5 + Hg + 2CH_3C\begin{matrix}=O\\ \diagdown H\end{matrix}$$

The reactions of o-ditolylmercury in chloroorganic solvents also take place much more rapidly than those of diphenylmercury.

In chloroform and 1,2-dichloroethane, o-tolylmercuric chloride and toluene are formed.

With chloroform, for example, we may write the reaction as follows:

$$(CH_3C_6H_4)_2Hg + 2CHCl_3 \xrightarrow{h\nu} C_6H_5CH_3 + CH_3C_6H_4HgCl +$$

$$+ \cdot CCl_3 + (\cdot CHCl_2)$$

$$2 \cdot CCl_3 \rightarrow Cl_3C - CCl_3.$$

In addition, a small quantity of mercury separates (not so small, however, as in the case of diphenylmercury).

In carbon tetrachloride, o-tolylmercuric chloride and o-chlorotoluene are formed:

$$(CH_3C_6H_4)_2Hg + 2CCl_4 \xrightarrow{h\nu} CH_3C_6H_4Cl + CH_3C_6H_4HgCl + 2 \cdot CCl_3$$

$$2 \cdot CCl_3 \rightarrow Cl_3C - CCl_3.$$

In carbon tetrachloride and in chloroform, hexachloroethane is always formed.

We must assume that the photoreaction of o-ditolylmercury takes place similarly

to that of diphenylmercury, i.e., that there takes place a preliminary dissociation of the o-ditolylmercury:

$$(CH_3C_6H_4)_2Hg \xrightarrow{h\nu} CH_3C_6H_4\cdot + CH_3C_6H_4Hg\cdot$$

As is obvious from the reactions given, the o-tolyl radical reacts with solvents exactly the way the phenyl radical does.

EXPERIMENTAL *

o-Ditolylmercury in Methanol

2 g of o-ditolylmercury in 10 ml of methyl alcohol was illuminated for 30 hours. 1.03 g of mercury (quantitative yield) separated out, but the color of the solution did not change. The alcohol was driven off, the distillate was diluted with water, and the insoluble part was nitrated in a solution of carbon tetrachloride. The nitro-compound appeared to be 2,4-dinitrotoluene, with m.p. 70° (after recrystallization from alcohol); there was no lowering of the m.p. upon mixing with the pure compound.

The alcoholic solution had a sharp formaldehyde odor, and gave the reactions for aldehydes (fuchsine-sulfurous acid, silver mirror).

o-Ditolylmercury and the Monoethyl Ether of Ethylene Glycol

1 g of o-ditolylmercury in 15 ml of the monoethyl ether of ethylene glycol was illuminated for 18 hours. The solution acquired the color of tea. The mercury filtered off weighed 0.52 g (quantitative yield). The filtrate was distilled, and the distillate diluted with water; the insoluble part of 0.5 ml was nitrated. The nitro product melted at 70° (after recrystallization from alcohol), and gave no m.p. lowering with pure 2,4-dinitrotoluene. The aqueous solution of the monoethyl ether of ethylene glycol had a sharp odor (acetaldehyde) and gave aldehyde reactions (mirror).

o-Ditolylmercury and Ethyl Formate

1.46 g of o-ditolylmercury in 10 ml of ethyl formate was illuminated for 18 hours. The solution acquired a pale yellow color. A quantitative yield of 0.75 g of mercury was obtained. The mercury was filtered off, and the solution diluted with water; the insoluble part, amounting to 0.5 ml, was nitrated. The nitro compound appeared to be 2,4-dinitrotoluene, with m.p. 70° (from alcohol); it gave no lowering of the melting point upon mixing with the pure compound.

The aqueous solution of ethyl formate gave the reactions for aldehyde (mirror).

o-Ditolylmercury and 1,2-Dichloroethane

1 g of o-ditolylmercury in 15 ml of 1,2-dichloroethane was illuminated for 12 hours. After only a half hour, the separation of mercury was noted. At the end of the reaction, the precipitate was filtered off and washed with hot dichloroethane. The mercury amounted to 0.36 g (69% of the theoretical).

The filtrate was distilled with steam. No unsaturated compounds were observed (bromine water).

The distillate was separated from water and nitrated; the weight of nitro compound was 0.5 g., its m.p. 70°; there was no lowering of the m.p. upon mixing with pure 2,4-dinitro compound. The residue from the distillation with steam was recrystallized from acetone; it weighed 0.27 g (31% of the theoretical), m.p. 141-142°, and gave no m.p. depression when mixed with pure o-tolylmercuric chloride.

o-Ditolylmercury and Chloroform

2 g of o-ditolylmercury in 10 ml of chloroform was illuminated for 15 hours.

*Student Vorobyeva took part in the experimental work.

The solution acquired a brown color. The precipitate was filtered off and washed with acetone, leaving 0.61 g of mercury (59% of the theoretical). From the acetone solution, 0.11 g of o-tolylmercuric chloride was obtained, m.p. 146°, no lowering of the m.p. when mixed with the pure compound. The filtrate was steam distilled; hexachloroethane was observed, with m.p. 186°, and no lowering of the m.p. upon mixing with the pure compound. The residue after distillation with steam was fractionally crystallized from acetone and alcohol to give 0.25 g of o-ditolylmercury (12.5% of the amount taken), with m.p. 107°, no depression of the m.p. upon mixing with the pure compound; the recrystallization also gave o-tolylmercuric chloride, 0.18 g; thus a total of 0.29 g of o-tolylmercuric chloride was obtained (17% of the theoretical).

After the steam distillation, the distillate was fractionated, and the residue nitrated. The nitro compound appeared to be 2,4-dinitrotoluene, with m.p. 70°, and gave no lowering of the melting point upon mixing with the pure compound.

o-Ditolylmercury and Carbon Tetrachloride

2 g of o-ditolylmercury in 15 ml of carbon tetrachloride was illuminated for 10 hours. The solution turned yellow. The precipitate was filtered off and recrystallized from alcohol; it had m.p. 146°, the latter not being lowered when mixed with pure o-tolylmercuric chloride, and weighed 1.35 g (79% of the theoretical). The filtrate was distilled with steam. Hexachloroethane crystallized out in the condenser. It had m.p. 186° in a sealed capillary; the m.p. was not depressed in a mixture with the pure compound.

The hexachloroethane was purified before the test by sublimation above sulfuric acid.

After the distillation with steam, 0.35 g (17.5% of the amount taken) of unreacted o-ditolylmercury was found in the residue; m.p. 107° (after recrystallization from acetone). Mixing with the pure substance gave no lowering.

The distillate was distilled on the water bath, leaving a colorless liquid in the residue. This was oxidized with an alkaline solution of permanganate to give o-chlorobenzoic acid with m.p. 140° (after recrystallization from hot water).

SUMMARY

1. A solution of o-ditolylmercury in carbon tetrachloride gives, upon illumination with ultraviolet light, o-tolylmercuric chloride, o-chlorotoluene, and hexachloroethane.

2. A solution of o-ditolylmercury in chloroform gives, upon illumination, mercury, o-tolylmercuric chloride, toluene, and hexachloroethane.

3. o-Ditolylmercury in 1,2-dichloroethane gives o-tolylmercuric chloride, mercury, and toluene.

4. In solvents that did not contain halogen (methanol, the monoethyl ether of ethylene glycol, and ethyl formate), photolysis of o-ditolylmercury always gave toluene, a quantitative yield of mercury, and aldehyde.

5. The tolyl radical obtained by photolysis of o-ditolylmercury reacts like the phenyl radical; however, the reaction takes place more rapidly, and with much greater separation of metallic mercury in chloroform and chloroethane.

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*See CB translation p. 71 ff.

THE SULFONATION AND THE SULFONIC ACIDS OF ACIDOPHOBIC COMPOUNDS

X. THE SULFONATION OF α-ACETYLFURAN

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In our previous works we have made a fundamental study of the action of pyridine-sulfotrioxide upon furan and its homologos [1], and only to a slight degree to touched on the sulfonation of furan derivatives. Thus, we attempted to sulfonate the methyl ether of furyl alcohol, furfural, and pyromucic acid [1].

The methyl ether of furyl alcohol tarred both under the direct action of pyridine-sulfotrioxide as well as in solvents (benzene, ether, dichloroethane). Furfural as a whole did not react, and after 10 hours of heating with pyridine-sulfotrioxide at 100° was recovered almost unchanged. Pyromucic acid reacted with pyridine-sulfotrioxide at a temperature of 140° with the loss of its carboxy group and the formation of furanmonosulfonic acid.

Up to the present, the sulfo derivatives of ketones of the furan series have not been described. We set out to study the sulfonation reaction of acetylfuran in order to confirm the rules stated by Rinkes about orientation in the furan series. By analogy with pyromucic acid [2] and acetylpyrrole [3], we could assume that its sulfonation could take place by the action of sulfuric acid or sulfuric anhydride.

Our experiments showed that under the action of sulfuric acid and sulfuric anhydride in dichloroethane, considerable blackening of the compound took place. After treatment of the sulfonated mass with a suspension of barium carbonate, it was impossible to isolate any considerable quantities of sulfonic acids. The sulfonation of acetylfuran with pyridine-sulfotrioxide proceeded under much more severe conditions than the usual sulfonation of furan compounds.

In order to make acetylfuran react, it was necessary to heat it at a temperature of 140° for 10 hours (usually, the sulfonation of furan and its homologs takes place almost quantitatively at 100°). But even under these conditions, acetylfuran does not react completely, and is partially recovered unchanged. An excess of pyridine-sulfotrioxide and the use of solvents did not increase the yield of sulfonated derivative. The yield of sulfoacetylfuran, calculated on the basis of all the acetylfuran used, reached 54%. Part of the acetylfuran being sulfonated was recovered unchanged, and calculating on the basis of the furan that reacted, the yield of sulfoacetylfuran reached 82.3%. Analysis of the sulfonated derivative corresponded to monosulfoacetylfuran.

In investigating the products of sulfonation, we did not note even traces of the disulfonic acid.

In the nitration of acetylfuran, the loss of the acetyl group has been noted, and the formation of nitrofuran along with the nitroacetylfuran [4]. A similar process takes place in the nitration of pyromucic acid [5].

In investigating the action of pyridine-sulfotrioxide on pyromucic acid, we observed that in this case, only substitution of the carboxyl group took place.

On the basis of all this, we have suggested that in the sulfonation of acetyl-

furan, the loss of the acetyl group may take place, even though only partially, and the formation of furan sulfonic acid. But in the investigation of the products of sulfonation we observed no furan sulfonic acid. The solution of the barium salt obtained by treatment with barium carbonate did not form the precipitate characteristic of furan sulfonic acid with S-benzylthiurone chloride.

Upon careful fractionation of the barium salt first obtained, it was impossible to isolate any furan sulfonic acid.

The positions of the sulfo groups were determined by the oxidation of the barium salt of sulfoacetylfuran with bromine water and chromate mixture. Even in the cold, bromine water caused the formation of a precipitate of barium sulfate. In view of the fact that the β-sulfonic acid group, as Hill and we ourselves have shown, [1,2], is stable to oxidants, the formation of barium sulfate in the oxidation is a demonstration of the α-position of the sulfonic acid group.

The formation of the β-isomer during the sulfonation of acetylfuran (by analogy with acetylpyrrole [8]) is improbable because of the orientation rules of the furan nucleus, as deduced by Rinkes [7]. As a result of detailed investigations of substitution reactions in the furan series, Rinkes considered that the formation of the β-isomer did not take place while the α-position was free. Despite this, we attempted to detect the β-isomer. For this purpose, we carried out the oxidation of the sulfoacetyl furan with chromate mixture. Among the products of oxidation, we did not succeed in detecting the presence of the sulfonic acid even qualitatively. This confirms the absence of any noticeable amounts of β-isomer.

EXPERIMENTAL

α-Acetylfuran was obtained by the method of Goldfarb and Smorgonsky [8], by the action of acetic-anhydride upon furan in benzene, in the presence of stannic chdloride:

M.p. 29.5°; n_D^{20} 1.5012.

Literature gives: m.p. 29° [8] ; n_D^{20} 1.5017 [8].

The Sulfonation of Acetylfuran

The sulfonation of acetyl furan was carried out by heating in sealed ampoules at a temperature of 140° for 10 to 12 hours. The sulfonated mass, a thick dark-brown oil, was treated with a suspension of barium carbonate and heated on a water bath (20 to 30 minutes). The hot solution was filtered through a Buchner funnel to remove barium sulfate and excess barium carbonate, and the precipitate washed with hot water. The filtrate was concentrated till crystals began to form, and the barium salt of acetylfuransulfonic acid was precipitated with alcohol. 2 g of acetylfuran and 5.8 g (1:2)of pyridine-sulfotrioxide gave 2.5 g of the barium salt of acetylfuransulfonic acid. Yield 53.5%, calculated on the total amount of acetylfuransulfonic used in the reaction. 2 g of acetylfuran and 8.5 g of pyridine-sulfotrioxide (1:3) gave 2.4 g of the barium salt of acetylfuransulfonic acid. Yield, 51.5%

2 g of acetylfuran, 5.8 g (1:2) of pyridine-sulfotrioxide, and 10 ml of dichloroethane were heated in an ampoule at a temperature of 140° for 10 hours. Before the usual treatment of the sulfonated mass with barium carbonate, the solution of dichdloroethane was poured off; after distillation of the dichloroethane, the liquid that remained went over at a temperature of 174-175°. There was thus recovered 0.8 g of unreacted acetylfuran. The sulfonated mass was treated in the usual way, and 2.5 g of the barium salt of the sulfonic acid of acetylfuran was obtained. The yield, based on the acetylfuran used up, was 82.5%. For purposes of analysis, the salt was recrystallized from a water-alcohol solution.

22.295 mg substance: 10.155 mg $BaSO_4$.

Found %: Ba 26.81.

$C_{12}H_{10}O_{10}S_2Ba$. Calculated %: Ba 26.63.

The solution of the barium salt, after treatment of the sulfonated mass with barium carbonate, gave no precipitate with S-benzylthiurone chloride; the formation of a precipitate is characteristic of α-furansulfonic acid.

Oxidation with Bromine Water. Even in the cold, bromine water produced a voluminous precipitate of barium sulfate from a solution of the barium salt of acetylfuransulfonic acid.

1 g of the barium salt of the sulfonic acid of acetylfuran was dissolved in 15 ml of water. The bromine water was added as long as the color of the bromine disappeared. The precipitate of barium sulfate was filtered off through a filter crucible. Then the precipitate was dried and roasted. Weight of barium sulfate: 0.32 g.

Oxidation with Chromate Mixture. To a solution of 1 g of the barium salt of acetylfuransulfonic acid, chromate mixture was added. The mixture was heated on a water bath for 30 minutes, and allowed to stand overnight. It was then treated with a paste of barium carbonate and boiled for 1.5 to 2 hours, until there was no chromate color in the filtrate. The filtrate was concentrated. The salt which remained after concentration was tested by fusion with metallic sodium for the presence of sulfur. No black precipitate of liver of sulfur was formed. Upon acidification, no odor of hydrogen sulfide was observed.

SUMMARY

1. By means of pyridine-sulfotrioxide, acetylfuran has been sulfonated for the first time with 82% yield.

2. The monosulfonic acid of acetylfuran has been obtained and analyzed in the form of its barium salt. The sulfonic acid obtained was 2-acetylfuransulfonic acid-5.

3. No perceptible quantities of the β-isomer of acetylfuran sulfonic acid have been observed.

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*See CB translation p. a591 ff.

THE INVESTIGATION OF THE SESQUITERPENE ALCOHOL "SHAIROL"

II. THE NUMBER OF DOUBLE BONDS IN SHAIROL

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Shairol was found in 1940 in the ethereal oil from the roots of Ferula pyramidata (Kar and Kir) Eug Kor.* According to previously published data [4,5], shairol is a sesquiterpene alcohol with the composition $C_{15}H_{28}O$, with m.p. 91-93°, and with a hydroxl group in a tertiary position, as can be deduced from the ease with which it splits off water upon heating with formic acid, and from its inability to form phthallic esters.

In the carbon skeleton of shairol there is doubtless a junction of the five- and seven-membered rings, in view of the fact that upon dehydrogenation shairol gives azulene, with the composition $C_{15}H_{18}$. The fact that shairol can be easily oxidized by potassium permanganate (during the oxidation the compounds $C_{15}H_{28}O_3$, with m.p. 221-223°, and $C_{15}H_{28}O_3$, with m.p. 102-103°, are formed; these have been partially investigated) leads to the conclusion that there is at least one double bond present in shairol. An indirect confirmation of this hypothesis is the formation during the dehydration of shairol of the hydrocarbon shairene, with two double bonds of which only one can have arisen by the splitting off of water, while the second double bond, apparently, was present in shairol (if we exclude the possibility of isomerization, which is probable, for example, in three-ringed alcohols). However, at the same time, direct experiments on hydrogenation have not succeeded in showing the presence of double bonds in shairol; this is assumed to be due to the peculiar position of the double bond, and the difficulty of its hydrogenation. In view of the need for more definite data on the number of double bonds in shairol, in order to decide whether the compound is monocyclic (in case there are two double bonds), bicyclic (in the case of a single double bond), or tricyclic (without double bonds), we undertook the experiments described below. It was found that with the use of PtO_2 in an amount of up to 30% of the weight of the shairol undergoing hydrogenation (previously, traces of catalyst had been used), there took place a comparatively rapid change of shairol into dihydroshairol, with the composition of $C_{15}H_{28}O$. Dihydroshairol is a colorless, viscous liquid, which gives no reaction with potassium permanganate or bromine. This shows that only a single double bond is present in shairol. As further evidence of the presence of the double bond in shairol, we have the experiment on the dehydration of dihydroshairol with formic acid, to give a hydrocarbon dihydroshairene, with the composition $C_{15}H_{26}$, and with a single double bond (molecular refraction data) formed by the splitting off of water. Upon the hydrogenation of dihydroshairene, the hydrocarbon tetrahydroshairene, with the composition $C_{15}H_{28}$, was obtained. This was a saturated compound (it gave no reaction for the double bond). The evidence indicated above is so definite that apparently no further confirmation is needed. None the less, we undertook to carry out experiments on the titration of shairol with benzoyl hydrogen peroxide. In accordance

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*Prof. E. P. Korovin in an illustrated monograph on the genus Ferula (press of the Acad. Sci. USSR, 1947) substituted the name Ferula pyramidata for Ferula ferulaeoides (Steud) Eug. Kor. comb. n.

with the investigations of N.A.Prilezhayev, S.S.Nametkin, B.A.Arbuzov, Bezeken, Meyervein, and other Russian and foreign investigators, [1,3] the oxidation of a molecule of an unsaturated compound containing a double bond, as a rule, requires the expenditure of an equimolecular amount of benzoyl hydrogen peroxide, with the formation of the corresponding oxide. The reaction is usually quantitative, and therefore has been proposed as a method for the determination of the number of double bonds in unsaturated compounds.

The oxidation of pure shairol (m.p. 91-93°) in a solution of chloroform by benzoyl hydrogen peroxide was carried out many times both at room temperature and below (-10°); it always led to the formation of a liquid, almost colorless, viscous product with n_D^{20} 1.4938 - 1.4940. The latter compound, according to the data of analysis, did not correspond to the oxide; it was stable to $KMnO_4$ in neutral acetone solution, and easily changed upon distillation in vacuum, or with steam at atmospheric pressure. Upon heating the substance with alkali, no alkali was consumed.

It is of interest to note that the oxidation of shairol with benzoyl hydrogen peroxide takes place very rapidly with considerable evolution of heat, and is usually completed in no more than 30 minutes. For the oxidation of a molecule of shairol, fewer than two molecules of the benzoyl hydrogen peroxide are required, and 80-95% more than one molecule.

These facts permit us to assume that the product of the oxidation of shairol by benzoyl hydrogen peroxide is a mixture of compounds with different oxygen content, probably the complete oxide, and unstable products of the peroxide type.

This assumption was partially confirmed by the fact that the action of $KMnO_4$ in acetone solution in a weakly alkaline medium on the product of the oxidation of shairol by benzoyl hydrogen peroxide gave a 25% yield of a substance with the composition $C_{15}H_{26}O_2$, m.p. 88-89.5°; this corrsponded to the composition and properties of shairol oxide.

The production of the monoxide of shairol was satisfactory evidence of the presence in shairol of one double bond. The unusual course of the oxidation of shairol by benzoyl hydrogen peroxide required an investigation of the mechanism of the reaction, and of the character of the substances formed during it, and could apparently be explained by a hypothesis about the specific peculiarity of the double bond. We might have arrived at this conclusion somewhat earlier on the basis of the formation from shairol, by oxidation with potassium permanganate in acetone solution, of two crystalline compounds, one of which had the carbon skeleton of a naphthalene derivative, and the other the carbon skeleton of an azulene derivative.

In connection with this work, we must note one more fact. According to the literature [6,8], the formation of a color with Br_2 in chloroform or acetic acid is considered specific for azulene-forming substances. Under the action of bromine, compounds with an azulene carbon skeleton give a blue or violet color. From the data on shairol, shairene, dihydroshairene, and the hydrogenated derivatives of these compounds, it follows that unsaturated compounds easily give the color reaction with Br_2. The hydrogenated compounds (dihydroshairol, tetrahydroshairene) do not give this reaction, or it is not characteristic (in acetic acid). Thus, the single satisfactory method of recognizing saturated compounds with an azulene skeleton at present is dehydrogenation which leads to the formation of typical azulenes. Saturated compounds of the azulene series cannot be distinguished by means of the known qualitative reactions.

EXPERIMENTAL

The Preparation and Properties of Dihydroshairol

1.2 g of PtO_2 (prepared according to the method of Adams [7]) was reduced with continuous agitation, in 5 ml of glacial acetic acid. Over a 10 minute period, 220 ml of hydrogen were required for the reduction. To the mixture obtained, there was added a solution of 4 g of shairol in 20 ml of glacial acetic acid. In the hydrogenation, which took 2 hours, 452 ml of hydrogen (20°, 765 mm) was used up, after which the consumption of hydrogen practically ceased. The velocity of hydrogenation at first amounted to 50-60 ml of H_2 in 10 minutes, and toward the end (after 1.5 hours) 2-3 ml in 10 minutes.

The solution was neutralized with soda and steam-distilled over a period of 1.5 to 3 hours. A colorless, viscous, oily liquid was isolated, in a quantity of 4.1 ml. The oil did not react with permanganate in acetone solution and did not crystallize even upon cooling to -15°. It was very soluble in ether, ethyl alcohol, and xylene, and insoluble in water.

B.p. 125-127° (3 mm); n_D^{20} 1.4932; d_{20}^{20} 0.9554; α_D^{14} + 16.8°; MR_D 68.11.

$C_{15}H_{28}O$. Calculated: MR_D 68.59.

0.1222 g substance: 0.3607 g CO_2; 0.1380 g H_2O.
Found %: C 80.50; H 12.54.
$C_{15}H_{28}O$. Calculated %: C 80.35; H 12.50.

Determination of hydroxyl according to the method of Chugayev and Tserevitinov (xylene solvent):

0.0666 g substance: 6.52 ml CH_4 (0°, 760 mm).
Found %: OH 7.5.
$C_{15}H_{27}OH$. Calculated %: OH 7.59.

The dihydroshairol obtained did not react with bromine in chloroform solution, and did not form any color (difference from shairol). In acetic acid solution dihydroshairol and bromine formed a blue solution only after prolonged action (not less than 2 hours).

The Preparation and Properties of Dihydroshairene

3.2 g of dihydroshairol was heated to boiling with 5 ml of 90% formic acid for 15 minutes. The solution was cooled, neutralized with soda, and steam-distilled. There quickly came over (15-20 minutes) a colorless, almost odorless hydrocarbon with the following characteristics (after distillation over Na):

B.p. 98-102° (3 mm); d_{20}^{20} 0.8982; n_D^{20} 1.4906; α_D^{15} + 18.84°; MR_D 66.38.

$C_{15}H_{28}F_1$. Calculated: MR_D 66.60.

0.0934 g substance: 0.2986 g CO_2; 0.1072 g H_2O.
Found %: C 87.19; H 12.75.
$C_{15}H_{28}$. Calculated %: C 87.38; H 12.62.

The dihydroshairene obtained reacted with bromine in chloroform or acetic acid solution, to give first a colorless product, which comparatively quickly acquired a blue color.

Dihydroshairene easily decolorized permanganate in acetone solution. It was very soluble in the usual solvents, slightly soluble in acetic acid, insoluble in water.

The Preparation and Properties of Tetrahydroshairene

Platinum oxide prepared according to the directions of Adams [7], in a quantity of 0.25 g, was mixed with 8 ml of glacial acetic acid and reduced with continuous

shaking. 54 ml of hydrogen was used up in the reduction. To the mixture was then added 1.3 g of dihydroshairene. The hydrogenation was completed in 50 minutes (17°, 768 mm), with 143 ml of hydrogen being consumed (required for 1 double bond, 141 ml). The solution was neutralized with dilute NaOH, and the oil distilled with steam. Yield 1.3 ml. The hydrocarbon which came over was distilled over Na and obtained in the form of a colorless liquid with the properties:

B.p. 83-86° (2-3 mm); d_{28}^{28} 0.8835; n_D^{20} 1.4788; α_D^{18} + 26.67°; MR_D 66.74.
$C_{15}H_{28}$. Calculated MR_D: 67.07.

0.1136 g substance: 0.3594 g CO_2; 0.1370 g H_2O.
0.0953 g substance: 0.3018 g CO_2; 0.1159 g H_2O.
Found %: C 86.26; 86.36; H 13.40, 13.51.
$C_{15}H_{28}$. Calculated %: C 86.54; H 13.46.

Tetrahydroshairene was unchanged in a chloroform solution of bromine; no violet or blue color was observed even after several days. Tetrahydroshairene colored an acetic acid solution of bromine a weak blue after 3 to 4 hours. In its solubility in different solvents, tetrahydroshairene did not differ from dihydroshairene.

The Action of Benzoyl Hydrogen Peroxide on Shairol

The titration of shairol with benzoyl hydrogen peroxide at room temperature: 1) 0.0442 g of shairol was dissolved in 5 ml of chloroform, and to the solution was gradually added 5 ml of 0.1 N solution of benzoyl hydrogen peroxide in chloroform. After 30 minutes, the excess of benzoyl hydrogen peroxide was titrated in the presence of KI in acetic acid with a 0.1 N thiosulfate solution. 3.55 ml of the 0.1 N benzoyl hydrogen peroxide solution was consumed during the oxidation.

Benzoyl hydrogen peroxide consumed..... 0.0524 g.
Benzoyl hydrogen peroxide calculated for one double bond..... 0.0278 g.
Benzoyl hydrogen peroxide calculated for two double bonds..... 0.0556 g.

2) 0.0514 g of shairol was oxidized as in the first experiment, but the excess of perbenzoic acid was titrated after 24 hours. The amount of 0.1 N perbenzoic acid used up in the oxidation was 4.3 ml.

Benzoyl hydrogen peroxide consumed..... 0.0593 g.
Benzoyl hydrogen peroxide calculated for one double bond..... 0.0319 g.
Benzoyl hydrogen peroxide calculated for two double bonds.... 0.0638 g.

The oxidation of shairol with perbenzoic acid at -10°. 3) 0.06 g of shairol was dissolved in 5 ml of chloroform, and the solution cooled to -10°. To it there was gradually added 10 ml of a solution of chloroform (cooled to -12°) containing 0.138 g of perbenzoic acid. After 30 minutes, a back titration required 4.8 ml of 0.1 N thiosulfate solution, i.e., the oxidation had consumed 5.2 ml of 0.1 N perbenzoic acid.

Perbenzoic acid consumed..... 0.0717 g.
Perbenzoic acid calculated for one double bond..... 0.0373 g.
Perbenzoic acid calculated for two double bonds..... 0.0746 g.

The oxidation of shairol with perbenzoic acid at -10° over a period of 24 hours gave results close to those described in experiment 3).

The oxidation of shairol with an amount of perbenzoic acid equivalent to one double bond led to incomplete oxidation.

4) 1 g of shairol was dissolved in 10 ml of chloroform and the solution cooled to -10°. To the solution was gradually added 13.5 ml of chloroform (cooled to -10°) containing 0.6356 g of perbenzoic acid (0.6216 g of perbenzoic acid was needed for a single double bond in 1 g of shairol). To avoid heating the mixture (the

temperature of the mixture could rise to -5°, and even to +2° upon rapid mixing of the solutions) the addition of the perbenzoic acid solution was carried out very carefully. Cooling kept it from going above -9°. At the end of the addition (this required 10 to 15 minutes) no perbenzoic acid was observed in the solution. The solution was shaken three times with 5% soda (until the benzoic acid had been completely removed), the chloroform was driven off in vacuum, and the residue dissolved in ethyl alcohol and diluted with water until the solution became cloudy. Needlelike crystals separated out to the amount of 0.4 g, with m.p. 91-92°; they gave no m.p. depression upon mixing with shairol. The residue which did not crystallize was concentrated to give a thick colorless liquid with n_D^{20} 1.4940.

5) The oxidation of shairol with perbenzoic acid used on a basis of more than two double bonds (1.4-1.48 g of perbenzoic acid per 1 g of shairol) was allowed to take place in chloroform at a temperature not below -5° for 30 minutes. After treatment of the solution with soda and removal of the solvent in vacuum, it gave a completely liquid product, either colorless or yellowish, with a neutral reaction and n_D^{20} 1.4938-1.4940.

Investigation of the Product Obtained with n_D^{20} 1.4940, By Oxidizing Shairol with Benzoyl Hydrogen Peroxide

1. It was observed that the action of a 3% solution of neutral potassium permanganate in acetone upon the substance produced no oxidatinn, and the permanganate was not decolorized.

2. Analysis gave the following data:

0.1154 g substance: 0.3101 g CO_2; 0.1102 g H_2O.
Found %: C 73.28; H 10.61.
$C_{15}H_{28}O_2$. Calculated %: C 75.63; H 10.92.
$C_{15}H_{28}O_3$. Calculated %: C 70.87; H 10.24.

From the analysis it was possible to conclude that the substance was neither the oxide nor the dioxide of shairol.

3. Distillation of the substance at 2 mm gave a product with b.p. 115-130°, n_D^{20} 1.5163, in the form of a thick dark-yellow liquid with a green tinge; it had an unsaturated character.

0.1314 g substance: 0.3791 g CO_2; 0.1202 g H_2O.
0.1297 g substance: 0.3736 g CO_2; 0.1198 g H_2O.
Found %: C 78.67, 78.55; H 10.16, 10.26.

Thus, distillation in vacuum produced a sharp change in the composition of the original substance.

4. Upon distillation of the substance with steam in neutral aqueous solution, there was obtained a good yield of product with n_D^{20} 1.5205; this product gave an intense violet color with bromine in acetic acid. This product was unsaturated (1 g of $KMnO_4$ was used up for 0.2 g of the product). Analysis gave the following results:

0.1062 g substance: 0.3100 g CO_2; 0.1040 g H_2O.
0.1128 g substance: 0.3297 g CO_2; 0.1105 g H_2O.
Found %: C 79.60, 79.71; H 10.88, 10.88.

Thus, even upon distillation of the substance with n_D^{20} 1.4940 with steam, there was a change. The amount of oxygen decreased, and double bonds appeared.

5. 0.1 g of the substance with n_D^{20} 1.4940 was heated for an hour at the boiling point in an alcoholic solution with 10 ml of 0.1 N KOH. At the end of the period, a back titration required 10 ml of 0.1 N H_2SO_4, i.e., no alkali was consumed,

but the product appeared unsaturated (easily decolorized permanganate).

These facts permit us to assume that the oxidation of shairol with benzoyl hydrogen peroxide gives an unstable product, possibly containing a substance of the peroxide type. However, in the product with n_D^{20} 1.4940, we also observed an oxide in the following, somewhat unusual manner.

The Action of Permanganate on the Product of the Oxidation of Shairol with Perbenzoic Acid

2 g of the product of the oxidation of shairol with perbenzoic acid with n_D^{20} 1.4940 was dissolved in 50 ml of acetone. To the solution there were added gradually, with shaking, 110 ml of 3% $KMnO_4$ and 5 ml of 0.1 N KOH. After 20 hours, long felt-like needles were observed in the solution; these were slightly soluble in aqueous acetone and aqueous alcohol. M.p. 88-89.5° (from aqueous alcohol). Yield 0.4-0.5 g. A mixed test with shairol gave a sharp lowering of the m.p.

0.1008 g substance: 0.2789 g CO_2; 0.0993 g H_2O.
0.0926 g substance: 0.2564 g CO_2; 0.0913 g H_2O.
Found %: C 75.46, 75.61; H 10.94, 10.95.
$C_{15}H_{28}O_2$. Calculated %: C 75.63; H 10.92.

Determination of hydroxyl by the method of Chugayev and Tserevitinov (xylene as solvent):

0.0426 g substance: 3.9 ml CH_4 (0°, 760 mm).
Found %: OH 6.94.
$C_{15}H_{25}O(OH)$. Calculated %: OH 7.14.

The substance liberated iodine from KI in acetic acid, and thus behaved like piperitone oxide, which had been studied by Williams and Balkovsky [2]. On the basis of its composition and properties, the substance seemed to be shairol oxide. It was not oxidized by permanganate, and with bromine in acetic acid solution formed a cherry-red color, which changed into an intense violet. The fact that shairol oxide was obtained confirmed the presence of one double bond in shairol.

SUMMARY

1. Shairol has only one double bond, as is shown by the following facts:

a) Shairol is hydrogenated in the presence of platinum black to give dihydroshairol, with the composition $C_{15}H_{28}O$;

b) The dehydration of dihydroshairol leads to the formation of a hydrocarbon with one double bond: dihydroshairene, with the composition $C_{15}H_{28}$;

c) The hydrogenation of dihydroshairene results in the saturated tetrahydroshairene, with the composition $C_{15}H_{28}$.

2. The oxidation of shairol with benzoyl hydrogen peroxide does not take place in the usual manner. For each molecule of shairol, 1.8 to 1.95 molecules of perbenzoic acid are consumed. The oxidation gives a liquid with n_D^{20} 1.4940, stable to $KMnO_4$ in acetone solution, but easily changed upon heating in vacuum or with steam. From this liquid, the action of permanganate in weakly alkaline acetone solution gives a substance with the composition $C_{15}H_{28}O_2$, with m.p. 88-89.5°, and the properties of a shairol oxide; this confirms the presence of one double bond in shairol. The greater part of the products of oxidation of shairol by perbenzoic acid remains of unknown nature, but in its properties it resembles compounds of the peroxide type.

3. Shairol and its unsaturated derivatives easily give a specific blue or violet color with bromine in chloroform or acetic acid solution. The hydrogenated derivatives of shairol do not give the color reaction with bromine, or give one

that is not characteristic.

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THE MECHANISM OF THE CONDENSATIONS OF ACID HALIDES WITH TERTIARY AMINES

III. THE REACTION OF BENZOYL CHLORIDE WITH 2-AMINOPYRIDINE

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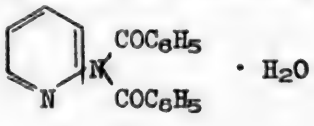
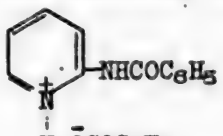
In our previous work [1], we have explained the role of water in the condensation of acid halides of carboxylic acids with tertiary amines, and have shown that in the presence of moisture, the complex first formed in the reaction decomposes to give the acid anhydride and the tertiary amine. In the present work, we have studied one of the specific instances of this reaction, that between benzoyl chloride and 2-aminopyridine in a pyridine medium containing water. It is known [2] that 2-aminopyridine reacts with benzoyl chloride to give mono- and dibenzoyl-2-aminopyridine. In carrying out this reaction in pyridine containing water, we had already isolated a substance with the empirical formula $C_{19}H_{16}O_3N_2$. As this compound differed from monobenzoyl-2-aminopyridine by one molecule of benzoic acid, and from dibenzoyl-2-aminopyridine by one molecule of water, we might suppose that its structure could be expressed by one of the following formulas:



(I)



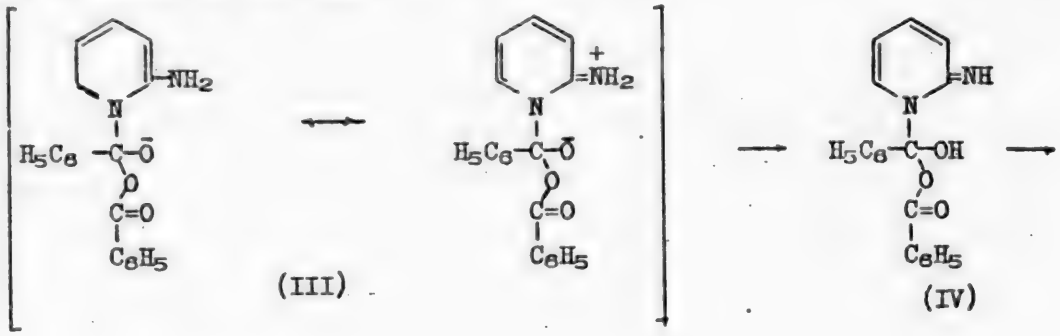
(II)

However, upon heating this substance in vacuum at 130°, benzoic acid split off, and not water, to give monobenzoyl-2-aminopyridine. The same products could be obtained by treating the substance in the cold with an alcoholic solution of hydrogen chloride. As under these conditions there is no change in dibenzoyl-2-aminopyridine, this gives us grounds to consider that formula (I) does not reflect the structure of our substance. The excellent solubility in ether, and the slight solubility in water are not characteristic properties of complexes of type (II). Attempts to obtain similar complexes from benzoic acid and monobenzoyl-2-aminopyridine did not give the desired results. Thus, the investigation of the properties of our substance forced us to discard structural formulas (I) and (II) and induced us to believe that it would be expedient to approach the determination of its structure by investigating the mechanism of its formation; we did this with the aid of several theoretical assumptions which had previously been shown to be of great help in a study of similar reactions.

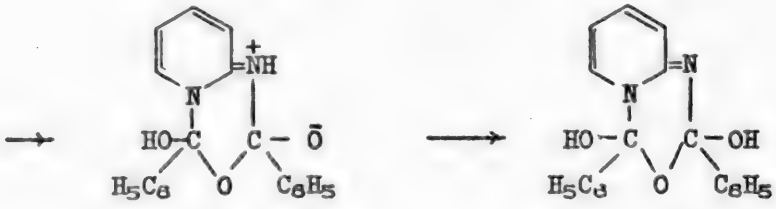
As has been indicated above, our substance was obtained only when moist pyridine was used as the reaction medium. In accordance with our previous work [1], the anhydrides of the carboxylic acids are obtained under these conditions. Consequently, in this case too we had to expect the formation of the anhydride of benzoic acid, which would then react with 2-aminopyridine. In order to confirm this supposition, we carried out the condensation of 2-aminopyridine with the anhydride of benzoic acid* in different solvents, and we thus obtained a substance similar in composition and properties to the substance which separated out during the condensation

*The anhydride of benzoic acid was obtained from benzoyl chloride and moist pyridine in yields from 75-85% of theory.

of benzoyl chloride with 2-aminopyridine in moist pyridine medium. These experiments confirmed the correctness of our hypothesis that 2-aminopyridine reacted not with the benzoyl chloride, but with the benzoyl anhydride. The condensation of these two reagents was favored by the possibility of resonance structures [3] arising in them. In the 2-aminopyridine molecule, the nitrogen atom in the heterocycle has one pair of free electrons, while several resonance structures have two pairs [3]; this favors its close approach to the molecule of benzoic anhydride, which has a positive carbon atom in several resonance structures, and this favors the occurrence of a reaction between the molecules; in its turn, the reaction leads to the formation of a complex of type III.



(III) (IV)



(V) (VI)

As a result of a transformation, connected with the process of dissociation and stabilization of this type of complex [1,4], a compound of type (IV) can be formed; this is a pyridonimine derivative. We attempted to show that the compound we had obtained had a pyridonimine grouping. The method of heating with alkali [5], which gives good results for alkyl derivatives of pyridonimine, was inapplicable, as upon heating with alkali the substance decomposed to give benzoic acid and aminopyridine. Precipitation with carbon dioxide [6] gave negative results.

One of the most convincing proofs of the existence of the pyridonimine structure is the formation of bicyclic compounds by the condensation of 2-aminopyridine with the esters of mono- and dialkylmalonic acids [7]. The reaction of 2-aminopyridine with benzoic anhydride, which we had under consideration, was very close in character to its reaction with the esters of malonic acid. A consideration of the mechanism of this reaction had already led us to a compound with formula (IV), whose resonance structures possessed the groups =NH= and $-C^{+}-O^{-}$, favorable to the formation of intramolecular complexes of type (V), and these, in the process of transformation customary for such complexes, would give compound (VI), i.e., a compound which contained two condensed rings and was a pyridonimine derivative. This formula corresponded to the empirical formula of the compound we had obtained, and completely explained its chemical properties.

Thus, having confirmed the formation of benzoic anhydride under the conditions of our reaction, and its ability to condense with 2-aminopyridine, we were able to give a theoretical analysis of the mechanism for the formation of the substance with

empirical formula $C_{19}H_{16}O_3N_2$, and arrived at the conclusion that formula (VI) corresponded to its structure.

EXPERIMENTAL

I. Monobenzoyl-2-aminopyridine

9.4 g of 2-aminopyridine was dissolved in 20 ml of absolutely dry pyridine and at 25°, 14 g of freshly distilled benzoyl chloride was slowly added. After all the acid chloride had been added, the reaction mixture was stirred at 25° for 1.5 to 2 hours. It was then poured into water. The crystals which precipitated out were filtered off, and crystallized from alcohol. Yield, 75% of theory. Melting point of monobenzoyl-2-aminopyridine 85-87°.

Found %: C 73.0; H 5.07.
$C_{12}H_{10}ON_2$. Calculated %: C 72.70; H 5.09.

II. Dibenzoyl-2-aminopyridine

The condensation of benzoyl chloride with 2-aminopyridine was carried out in a medium of acetone, ether, and 10% caustic soda. 9.4 g of 2-aminopyridine was dissolved in 25 ml of dry acetone, and at 26°, 28 g of freshly distilled benzoyl chloride was added. Two layers were formed. Agitation was continued at 30-35° for 2 hours. The mixture was then poured into water, and the precipitate filtered off and washed with water. It was recrystallized from alcohol in the form of white, glistening needles. It was slightly soluble in alcohol and ether, insoluble in water. M.p. 167-169°, yield 60% of theory.

Found %: C 75.22; H 4.89; N 9.35.
$C_{19}H_{14}O_2N_2$. Calculated %: C 75.46; H 4.67; N 9.27.

Dibenzoyl-2-aminopyridine was subjected to the following treatment:

a) Heating in vacuum for 6 hours at 130°. The substance was unchanged. M.p. 167-169°.

Found %: C 75.61; H 4.69.
$C_{19}H_{14}O_2N_2$. Calculated %: C 75.46; H 4.67.

b) Dibenzoyl-2-aminopyridine was dissolved in a five-fold quantity of a 10% alcoholic solution of hydrogen chloride. Dry ether was added to this solution until there was complete precipitation. The precipitated crystals of dibenzoyl-2-aminopyridine hydrochloride were filtered, washed with dry ether, and dissolved in a small quantity of water. The solution was neutralized with a 2% solution of soda. Crystals with m.p. 167-167.5° precipitated, i.e., they were the original dibenzoyl--2-aminopyridine.

Found %: N 9.66.
$C_{19}H_{14}O_2N_2$. Calculated %: N 9.27.

III. The Condensation of Benzoyl Chloride with 2-Aminopyridine in Moist Pyridine Medium

4.8 g of 2-aminopyridine was dissolved in 20 ml of moist pyridine (3 to 5% water). The solution was heated to 25° and slowly, with good agitation, 7 g of benzoyl chloride was added. Agitation continued at this temperature for 1.5 to 2 hours. The mixture was then poured into a 1% solution of hydrochloric acid. An oil precipitated; after cooling, this gradually crystallized. This was extracted with ether and the extract dried over sodium sulfate. The ether was distilled off, and the residue crystallized three times from alcohol. Yield of compound (VI) 40 to 50% of theory. Long white needles, easily soluble in alcohol and ether, slightly soluble in water. M.p. 89-90°.

Found %: C 71.39; H 5.28; N 8.66.
$C_{19}H_{16}O_3N_2$. Calculated %: C 71.22; H 5.04; N 8.74.

The substance underwent the following treatment:

a) Heating in vacuum. 1 g of the substance was heated in vacuum at 130° (oil bath temperature) for 6 hours. After an hour, crystals of benzoic acid already began to appear in the lead-off tube. A dense white mass remained in the flask. It was recrystallized twice from alcohol. The monobenzoyl-2-aminopyridine obtained melted at 85-87°.

Found %: C 72.83; H 5.15.
$C_{12}H_{10}ON_2$. Calculated %: C 72.70; H 5.09.

b) Heating with water. The substance was boiled in water for 8 hours, and filtered. It was then crystallized twice from alcohol. The substance obtained for analysis had m.p. 85-86°, and corresponded to monobenzoyl-2-aminopyridine.

Found %: C 73.17; H 5.26.
$C_{12}H_{10}ON_2$. Calculated %: C 72.70; H 5.09.

Alkali was added to the filtrate until the reaction was neutral; the solution was then evaporated to dryness. The sodium salt was dissolved in a minimal amount of water and carefully neutralized with hydrochloric acid. The benzoic acid which precipitated was crystallized from alcohol. It melted at 121-122°, and gave no m.p. lowering in a mixed test with known benzoic acid.

c) Treatment with an alcoholic solution of hydrogen chloride. 2 g of the substance was dissolved in 10 ml of a 10% alcoholic solution of hydrogen chloride. A transparent solution was obtained. Dry ether was added until precipitation was complete. Crystals sometimes precipitated; more often, an oil separated. The substance was dissolved in a small amount of water and neutralized with sodium bicarbonate. White crystals of monobenzoyl-2-aminopyridine precipitated. They were filtered off and crystallized from alcohol. M.p. 85-87°.

Found %: N 14.32.
$C_{12}H_{10}ON_2$. Calculated %: N 14.14.

d) Treatment with picric acid. 1 g of the substance was dissolved in alcohol and to the hot solution was added a hot saturated alcoholic solution of picric acid. Clear yellow crystals at once precipitated out. These were filtered, washed many times with alcohol, and crystallized twice from alcohol. The melting point of the monobenzoyl-2-aminopyridine picrate was 196-197°.

Found %: N 16.6.
$C_{18}H_{13}O_8N_5$. Calculated %: N 16.39.

IV. The Condensation of Benzoic Anhydride with 2-Aminopyridine

a) In pyridine medium. 3.3 g of 2-aminopyridine was dissolved in 15 g of pyridine and heated to 26°; 8.5 g of benzoic anhydride was gradually added while good agitation was maintained. The temperature slowly rose. After the addition of all the anhydride, the reaction mixture was agitated for 2 hours at a temperature of 40-50°. It was then poured into water, and extracted with ether. The ether was driven off, and the residue twice recrystallized from alcohol. Yield 60%. White needles, with m.p. 89-90°.

Found %: C 71.01; H 5.03; N 8.51.
$C_{19}H_{16}O_3N_2$. Calculated %: C 71.22; H 5.04; N 8.74.

b) The experiment was carried out under the conditions of (IV, a), but acetone was used as a medium instead of pyridine. Yellowish needles, with m.p. 89-90°.

Found %: N 8.81.
$C_{19}H_{18}O_3N_2$. Calculated %: N 8.74.

The melting point and analysis of the substance obtained in experiments IV, a and IV,b, showed that it was similar to the substance obtained in experiment III.

SUMMARY

1. The condensation of benzoyl chloride with 2-aminopyridine in moist pyridine medium gives a new substance with the empirical formula $C_{19}H_{18}O_3N_2$.

2. It has been shown that in moist pyridine medium, the reaction takes place not between benzoyl chloride and 2-aminopyridine, but between the latter and benzoic anhydride.

3. The substance with the empirical formula $C_{19}H_{18}O_3N_2$ is a bicyclic derivative of pyridonimine.

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COMPETITION FOR PRIZES OF THE USSR ACADEMY OF SCIENCES IN 1950

The Division of Chemical Sciences of the USSR Academy of Sciences announces that the following prizes of the USSR Academy of Sciences will be awarded in 1950.

1. S.V.Lebedev Prizes. – One prize of 15,000 rubles and two prizes of 5,000 rubles each for the best scientific papers in the field of synthetic rubber.
Date for submission of papers: March 1, 1950.

2. D.I.Mendelyeev Prizes – Two prizes of 20,000 rubles each and two prizes of 10,000 rubles each for original theoretical research and scientific papers of high practical value in chemistry and physics.
Date for submission of papers: November 1, 1950.

3. N.S. Kurnakov Prize – 10,000 rubles for an outstanding paper in the field of inorganic chemistry, physico-chemical analysis, or their application.
Date for submission of papers: August 1, 1950.

4. L.A.Chugayev Prize – 10,000 rubles for the best paper on chemistry.
Date for submission of papers: June 15, 1950.

5. N.D.Zelinsky Prize – 10,000 rubles for an outstanding paper in the field of organic chemistry and the chemistry of petroleum.
Date for submission of papers: September 1, 1950.

6. A.E.Porai-Koshits Prize – 10,000 rubles for the best research paper in the field of the chemistry and technology of dyes and organic intermediates.
Date for submission of papers: June 1, 1950.

Papers submitted in competition for the above prizes should be addressed to the Division of Chemical Sciences, USSR Academy of Sciences, Moscow, Bolshaya Kaluzhskaya 31.

Prizes will be awarded by the Presidium of the USSR Academy of Sciences to Soviet citizens, groups thereof as collective authors, and Soviet scientific institutions.

Papers submitted in competition for the above prizes may be submitted by scientific societies, research institutes, institutions of higher learning, governmental departments, social organizations, and private individuals.

Papers in competition for the prizes are to be submitted in Russian, in three copies, typewritten or printed, with the legend: "Submitted in competition for the .....Prize".

Papers submitted in competition for prizes must be accompanied by brief biographical data on the author, listing his principal scientific papers and inventions.

Division of Chemical Sciences,
USSR Academy of Sciences.